

Connecting via Winsock to STN

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LOGINID : SSSPTA1600BYA

PASSWORD:

TERMINAL (ENTER 1, 2, 3 OR 3):

* * * * * * * * * * Welcome to STN International * * * * * * * * * *

NEWS 1 Web Page URLs for STN Seminar Schedule - N. America
NEWS 2 "Ask CAS" for self-help around the clock
NEWS 3 DEC 05 CASREACT(R) - Over 10 million reactions available
NEWS 4 DEC 14 2006 MeSH terms loaded in MEDLINE/LMEDLINE
NEWS 5 DEC 14 2006 MeSH terms loaded for MEDLINE file segment of TOXCENTER
NEWS 6 DEC 14 CA/CAplus to be enhanced with updated IPC codes
NEWS 7 DEC 21 IPC search and display fields enhanced in CA/CAplus with the
IPC reform
NEWS 8 DEC 23 New IPC8 SEARCH, DISPLAY, and SELECT fields in USPATFULL/
USPAT2
NEWS 9 JAN 13 IPC 8 searching in IFIPAT, IFIUDB, and IFICDB
NEWS 10 JAN 13 New IPC 8 SEARCH, DISPLAY, and SELECT enhancements added to
INPADOC
NEWS 11 JAN 17 Pre-1988 INPI data added to MARPAT
NEWS 12 JAN 17 IPC 8 in the WPI family of databases including WPIFV

NEWS EXPRESS JANUARY 03 CURRENT VERSION FOR WINDOWS IS V8.01,
CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
AND CURRENT DISCOVER FILE IS DATED 19 DECEMBER 2005.
V8.0 USERS CAN OBTAIN THE UPGRADE TO V8.01 AT
<http://download.cas.org/express/v8.0-Discover/>

NEWS HOURS STN Operating Hours Plus Help Desk Availability
NEWS INTER General Internet Information
NEWS LOGIN Welcome Banner and News Items
NEWS PHONE Direct Dial and Telecommunication Network Access to STN
NEWS WWW CAS World Wide Web Site (general information)

Enter NEWS followed by the item number or name to see news on that specific topic.

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* STN_Columbus_000

FILE 'HOME' ENTERED AT 05:55:34 ON 20 JAN 2006

=> fil reg
COST IN U.S. DOLLARS

| SINCE FILE
ENTRY | TOTAL
SESSION |
|---------------------|------------------|
| 0.21 | 0.21 |

FILE 'REGISTRY' ENTERED AT 05:55:52 ON 20 JAN 2006
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
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STRUCTURE FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2
DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

Please note that search-term pricing does apply when conducting SmartSELECT searches.

*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
*

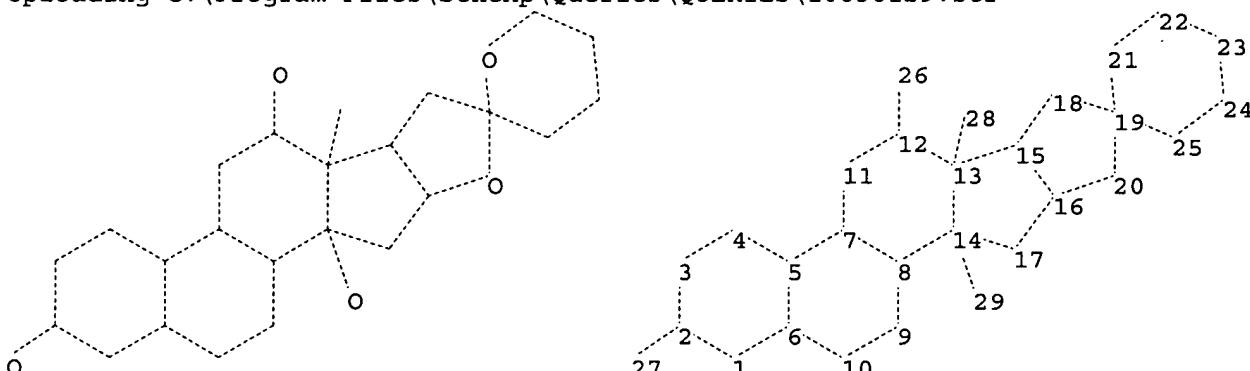
Structure search iteration limits have been increased. See HELP SLIMITS for details.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=>

Uploading C:\Program Files\Stnexp\Queries\QUERIES\10636129.str



chain nodes :

26 27 28 29

ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
24 25

chain bonds :

2-27 12-26 13-28 14-29

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12 12-13
13-14 13-15 14-17 15-16 15-18 16-17 16-20 18-19 19-20 19-21 19-25 21-22
22-23 23-24 24-25

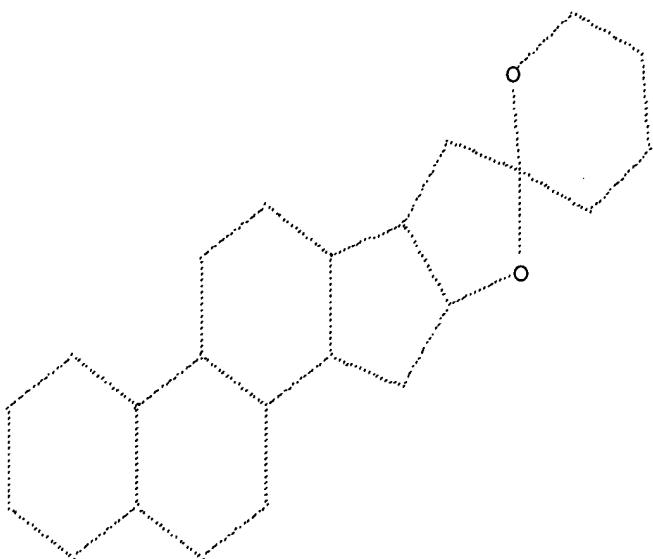
exact/norm bonds :

1-2 1-6 2-3 2-27 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12
12-13 12-26 13-14 13-15 13-28 14-17 14-29 15-16 15-18 16-17 16-20 18-19
19-20 19-21 19-25 21-22 22-23 23-24 24-25

```
Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:Atom 26:CLASS 27:CLASS 28:CLASS
29:CLASS
```

```
L1      STRUCTURE UPLOADED
```

```
=> d
L1 HAS NO ANSWERS
L1      STR
```



```
Structure attributes must be viewed using STN Express query preparation.
```

```
=> s 11
SAMPLE SEARCH INITIATED 05:56:22 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -    775 TO ITERATE
```

```
100.0% PROCESSED      775 ITERATIONS          50 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01
```

```
FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:    13830 TO    17170
PROJECTED ANSWERS:       4907 TO     6973
```

```
L2      50 SEA SSS SAM L1
```

```
=> s 11 full
FULL SEARCH INITIATED 05:56:28 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -    16041 TO ITERATE
```

```
100.0% PROCESSED      16041 ITERATIONS        6478 ANSWERS
SEARCH TIME: 00.00.01
```

```
L3      6478 SEA SSS FUL L1
```

```
=> fil stnguide
COST IN U.S. DOLLARS          SINCE FILE      TOTAL
                                ENTRY        SESSION
FULL ESTIMATED COST          166.94       167.15
```

FILE 'STNGUIDE' ENTERED AT 05:56:32 ON 20 JAN 2006
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 AND TECHNOLOGY CORPORATION, AND FACHINFORMATIONSZENTRUM KARLSRUHE

FILE CONTAINS CURRENT INFORMATION.
 LAST RELOADED: Jan 13, 2006 (20060113/UP).

```
=> fil reg
COST IN U.S. DOLLARS          SINCE FILE      TOTAL
                                ENTRY        SESSION
FULL ESTIMATED COST          0.12         167.27
```

FILE 'REGISTRY' ENTERED AT 05:57:33 ON 20 JAN 2006
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STRUCTURE FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2
 DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

Please note that search-term pricing does apply when
 conducting SmartSELECT searches.

```
*****
*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added,   *
* effective March 20, 2005. A new display format, IDERL, is now     *
* available and contains the CA role and document type information. *
*****
*****
```

Structure search iteration limits have been increased. See HELP SLIMITS
 for details.

REGISTRY includes numerically searchable data for experimental and
 predicted properties as well as tags indicating availability of
 experimental property data in the original document. For information
 on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=> d his

(FILE 'HOME' ENTERED AT 05:55:34 ON 20 JAN 2006)

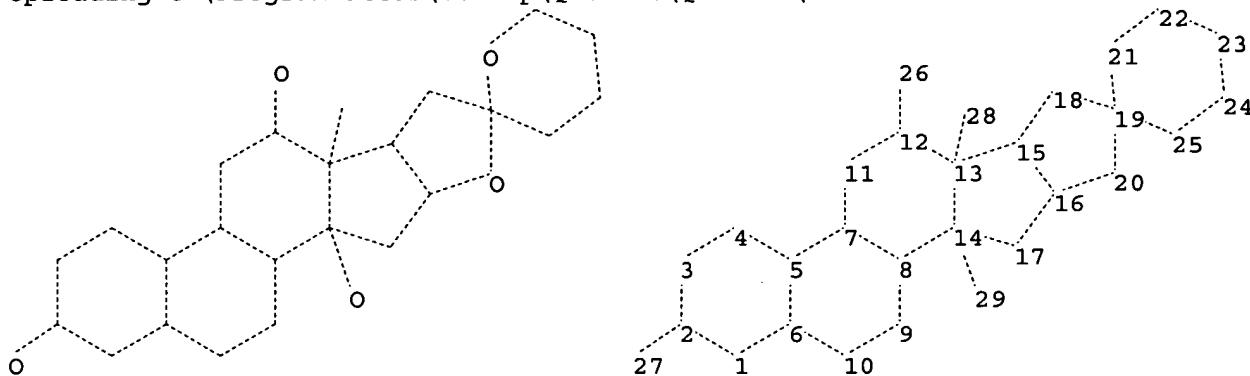
FILE 'REGISTRY' ENTERED AT 05:55:52 ON 20 JAN 2006
 L1 STRUCTURE uploaded
 L2 50 S L1
 L3 6478 S L1 FULL

FILE 'STNGUIDE' ENTERED AT 05:56:32 ON 20 JAN 2006

FILE 'REGISTRY' ENTERED AT 05:57:33 ON 20 JAN 2006

=>

Uploading C:\Program Files\Stnexp\Queries\QUERIES\10636129.str



chain nodes :

26 27 28 29

ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
24 25

chain bonds :

2-27 12-26 13-28 14-29

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12 12-13
13-14 13-15 14-17 15-16 15-18 16-17 16-20 18-19 19-20 19-21 19-25 21-22
22-23 23-24 24-25

exact/norm bonds :

1-2 1-6 2-3 2-27 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12
12-13 12-26 13-14 13-15 13-28 14-17 14-29 15-16 15-18 16-17 16-20 18-19
19-20 19-21 19-25 21-22 22-23 23-24 24-25

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:Atom 26:CLASS 27:CLASS 28:CLASS
29:CLASS

L4 STRUCTURE UPLOADED

=> d

L4 HAS NO ANSWERS

L4 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> s 14 subset=13 full

FULL SUBSET SEARCH INITIATED 05:57:58 FILE 'REGISTRY'
FULL SUBSET SCREEN SEARCH COMPLETED - 34 TO ITERATE

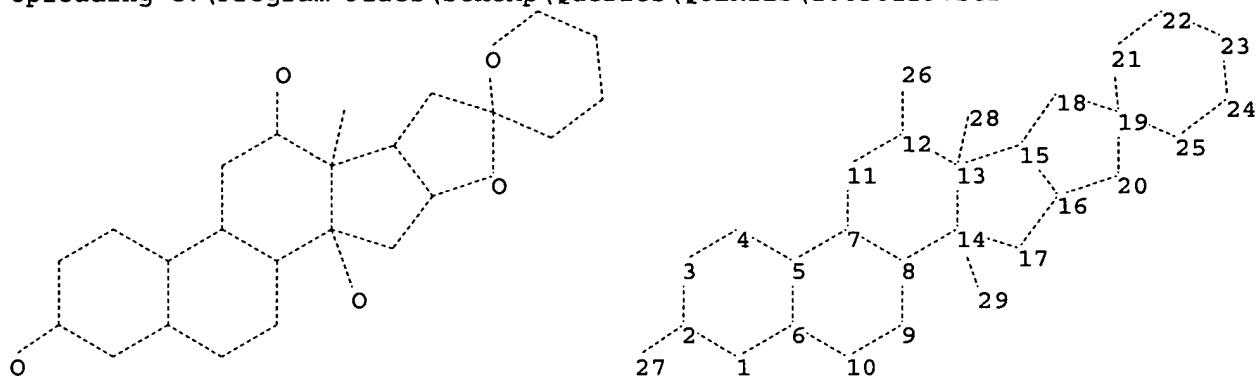
100.0% PROCESSED 34 ITERATIONS
SEARCH TIME: 00.00.01

0 ANSWERS

L5 0 SEA SUB=L3 SSS FUL L4

=>

Uploading C:\Program Files\Stnexp\Queries\QUERIES\10636129.str



chain nodes :

26 27 28 29

ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
24 25

chain bonds :

2-27 12-26 13-28 14-29

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12 12-13
13-14 13-15 14-17 15-16 15-18 16-17 16-20 18-19 19-20 19-21 19-25 21-22

22-23 23-24 24-25

exact/norm bonds :

1-2 1-6 2-3 2-27 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12
12-13 12-26 13-14 13-15 13-28 14-17 14-29 15-16 15-18 16-17 16-20 18-19
19-20 19-21 19-25 21-22 22-23 23-24 24-25

Match level :

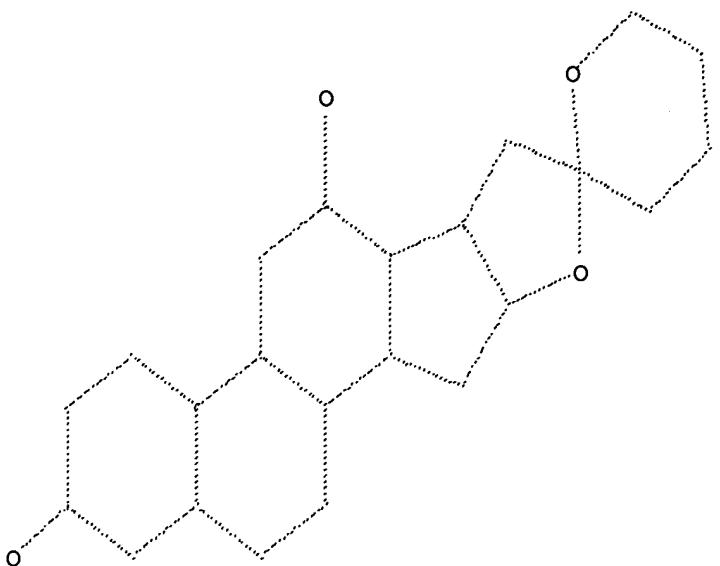
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:Atom 26:CLASS 27:CLASS 28:CLASS
29:CLASS

L6 STRUCTURE UPLOADED

=> d

L6 HAS NO ANSWERS

L6 STR



Structure attributes must be viewed using STN Express query preparation.

```
=> s 16 subset=13 full
FULL SUBSET SEARCH INITIATED 05:59:07 FILE 'REGISTRY'
FULL SUBSET SCREEN SEARCH COMPLETED - 3417 TO ITERATE

100.0% PROCESSED 3417 ITERATIONS 935 ANSWERS
SEARCH TIME: 00.00.01
```

L7 935 SEA SUB=L3 SSS FUL L6

```
=> s 17 and caplus/lc
49389268 CAPLUS/LC
L8 844 L7 AND CAPLUS/LC
```

| | | | |
|---------------------------|------------|---------|--|
| => fil stnguide | | | |
| COST IN U.S. DOLLARS | SINCE FILE | TOTAL | |
| | ENTRY | SESSION | |
| FULL ESTIMATED COST | 84.88 | 252.15 | |

FILE 'STNGUIDE' ENTERED AT 05:59:18 ON 20 JAN 2006
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 AND TECHNOLOGY CORPORATION, AND FACHINFORMATIONSZENTRUM KARLSRUHE

FILE CONTAINS CURRENT INFORMATION.
 LAST RELOADED: Jan 13, 2006 (20060113/UP).

| | | | |
|----------------------|------------|---------|--|
| => fil reg | | | |
| COST IN U.S. DOLLARS | SINCE FILE | TOTAL | |
| | ENTRY | SESSION | |
| FULL ESTIMATED COST | 0.12 | 252.27 | |

FILE 'REGISTRY' ENTERED AT 06:00:12 ON 20 JAN 2006
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DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

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*
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* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
*

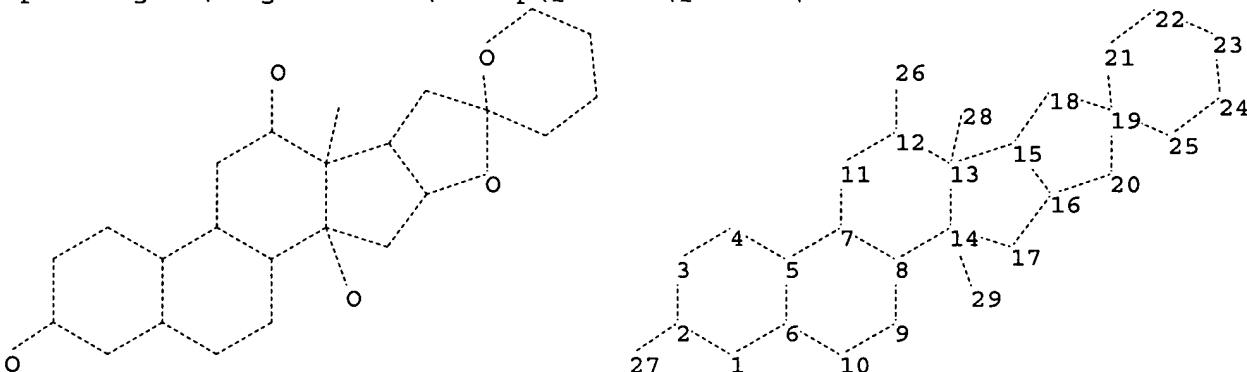
Structure search iteration limits have been increased. See HELP SLIMITS for details.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=>

Uploading C:\Program Files\Stnexp\Queries\QUERIES\10636129.str



chain nodes :
26 27 28 29
ring nodes :
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
24 25
chain bonds :
2-27 12-26 13-28 14-29
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12 12-13
13-14 13-15 14-17 15-16 15-18 16-17 16-20 18-19 19-20 19-21 19-25 21-22
22-23 23-24 24-25
exact/norm bonds :
1-2 1-6 2-3 2-27 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12
12-13 12-26 13-14 13-15 13-28 14-17 14-29 15-16 15-18 16-17 16-20 18-19
19-20 19-21 19-25 21-22 22-23 23-24 24-25

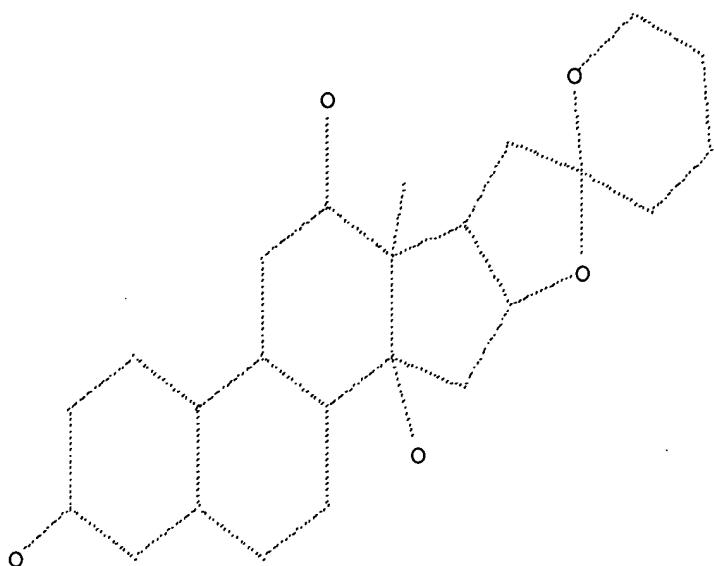
```
Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:Atom 26:CLASS 27:CLASS 28:CLASS
29:CLASS
```

```
L9      STRUCTURE UPLOADED
```

```
=> d
```

```
L9 HAS NO ANSWERS
```

```
L9      STR
```



```
Structure attributes must be viewed using STN Express query preparation.
```

```
=> d his
```

```
(FILE 'HOME' ENTERED AT 05:55:34 ON 20 JAN 2006)
```

```
FILE 'REGISTRY' ENTERED AT 05:55:52 ON 20 JAN 2006
```

```
L1      STRUCTURE UPLOADED
```

```
L2      50 S L1
```

```
L3      6478 S L1 FULL
```

```
FILE 'STNGUIDE' ENTERED AT 05:56:32 ON 20 JAN 2006
```

```
FILE 'REGISTRY' ENTERED AT 05:57:33 ON 20 JAN 2006
```

```
L4      STRUCTURE UPLOADED
```

```
L5      0 S L4 FULL SUB=L3
```

```
L6      STRUCTURE UPLOADED
```

```
L7      935 S L6 FULL SUB=L3
```

```
L8      844 S L7 AND CAPLUS/LC
```

```
FILE 'STNGUIDE' ENTERED AT 05:59:18 ON 20 JAN 2006
```

```
FILE 'REGISTRY' ENTERED AT 06:00:12 ON 20 JAN 2006
```

```
L9      STRUCTURE UPLOADED
```

```
=> s 19 subset=l7 full
```

FULL SUBSET SEARCH INITIATED 06:00:51 FILE 'REGISTRY'
FULL SUBSET SCREEN SEARCH COMPLETED - 77 TO ITERATE

100.0% PROCESSED 77 ITERATIONS 22 ANSWERS
SEARCH TIME: 00.00.01

L10 22 SEA SUB=L7 SSS FUL L9

=> s l10 and caplus/lc

49389268 CAPLUS/LC

L11 21 L10 AND CAPLUS/LC

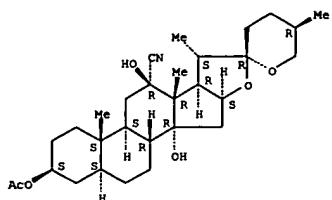
=> s l10 not l11

L12 1 L10 NOT L11

=> d

L12 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2006 ACS on STN
RN 6875-59-8 REGISTRY
ED Entered STN: 16 Nov 1984
CN 5 α -Spirostan-12 α -carbonitrile, 3 β ,12 β ,14-trihydroxy-, 3-acetate, (25R)- (8CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C30 H45 N O6

Absolute stereochemistry.



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

=> fil caplus
COST IN U.S. DOLLARS
FULL ESTIMATED COST

| SINCE FILE ENTRY | TOTAL SESSION |
|------------------|---------------|
| 46.94 | 299.21 |

FILE 'CAPLUS' ENTERED AT 06:01:12 ON 20 JAN 2006
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FILE COVERS 1907 - 20 Jan 2006 VOL 144 ISS 4
FILE LAST UPDATED: 18 Jan 2006 (20060118/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

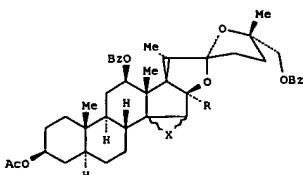
<http://www.cas.org/infopolicy.html>

=> s 111
L13 13 L11
=> d ibib abs hitstr 1-13

L13 ANSWER 1 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:372938 CAPLUS
 DOCUMENT NUMBER: 140:391402
 TITLE: Catalytic oxidation of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers
 INVENTOR(S): Fuchs, Philip; Lee, Seongmin
 PATENT ASSIGNEE(S): USA
 SOURCE: U.S. Pat. Appl. Publ., 38 pp.
 CODEN: USXXCO
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|------|----------|-----------------|------------|
| US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |
| PRIORITY APPLN. INFO.: | | | US 2002-403498P | P 20020814 |

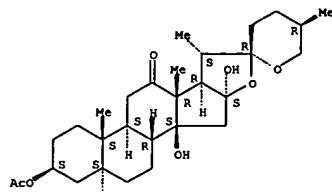
OTHER SOURCE(S): CASREACT 140:391402
 GI



AB The invention provides a catalytic, chemospecific and stereospecific method of oxidizing a wide variety of substrates without unwanted side reactions. Essentially, the method of the instant invention, under relatively mild reaction conditions, catalytically, stereospecifically and chemospecifically inserts oxygen into a hydrocarbon C-H bond. Oxidation (oxygen insertion) at a tertiary C-H bond to form an alc. (and in some cases a hemiacetal) at the tertiary carbon is favored. The stereochemistry of an oxidized tertiary carbon is preserved. Ketones are formed by oxidizing a secondary C-H bond and ring-cleaved diones are formed by oxidizing tertiary CH bonds. Thus, epoxycalc. I ($X = O$, $R = OH$) was prepared by reacting spiroketal compound I ($X = \text{bond}$, $R = H$) in an anhydrous solvent with chromium (VI) oxidant and a co-oxidant at a reaction temperature between about -100° C to about 0° C and a reaction time of between about 30 min to about 3 h. The method is useful in the synthesis of intermediates appropriate for preparation of analogs of the

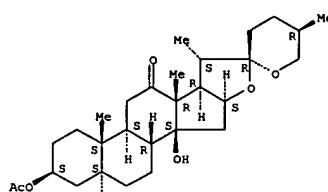
L13 ANSWER 1 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)
 cephalostatin/ritterazine family of marine natural products.
 IT 571185-76-7P
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
 (catalytic oxidation of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers)
 RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 78216-38-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (catalytic oxidation of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers)
 RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

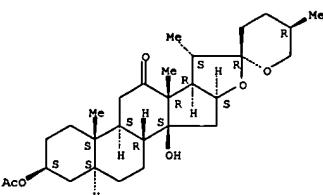


L13 ANSWER 2 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:261227 CAPLUS
 DOCUMENT NUMBER: 140:423861
 TITLE: An Efficient C-H Oxidation Protocol for α -Hydroxylation of Cyclic Steroidal Ethers
 AUTHOR(S): Lee, Seongmin; Fuchs, Philip L.
 CORPORATE SOURCE: Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA
 SOURCE: Organic Letters (2004), 6(9), 1437-1440
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 140:423861
 AB Various C-16 hydroxy steroids have been prepared with the aid of CrO₃/Bu₄NIO₄. Out of the two possible reaction courses, transition state B is favored because of less steric interference between substrate and CrO₄. Thus, C-H bonds at C-16 are oxidized selectively.

IT 78216-38-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (regio-, stereo- and chemoselective α -hydroxylation of cyclic steroidal ethers using CrO₃/Bu₄NIO₄)

RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



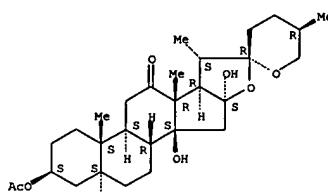
IT 571185-76-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (regio-, stereo- and chemoselective α -hydroxylation of cyclic steroidal ethers using CrO₃/Bu₄NIO₄)

RN 571185-76-7 CAPLUS

CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

L13 ANSWER 2 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)



REFERENCE COUNT: 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE REFORMAT

ACCESSION NUMBER: 2003:555356 CAPLUS

DOCUMENT NUMBER: 139:377920

TITLE: Diospolysaponin A, a new polyoxygenated spirostanol saponin from the tubers of *Dioscorea polygonoides* Osorio, Jaime Nino; Mosquera Martinez, Oscar M.; Correa Navarro, Yaned M.; Mimaki, Yoshihiro;

AUTHOR(S): Sakagami,

CORPORATE SOURCE: Hiroshi; Sashida, Yutaka
Laboratorio de Biotecnologia-Productos Naturales,
Escuela de Tecnologia Quimica, Universidad

Tecnologica

de Pereira, La Julita, Pereira, Colombia
Heterocycles (2003), 60(7), 1709-1715

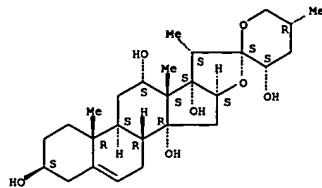
SOURCE: CODEN: HETCYAM; ISSN: 0385-5414

PUBLISHER: Japan Institute of Heterocyclic Chemistry

DOCUMENT TYPE: Journal

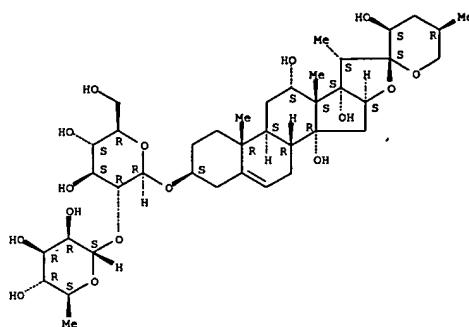
LANGUAGE: English

GI



RN 623939-65-1 CAPLUS
 CN Spirost-5-ene-12,14,17,23-tetrol, 3-([2-O-(6-deoxy-a-L-mannopyranosyl)-β-D-glucopyranosyl]oxy)-, (3β,12α,23S,25R)-(9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Chemical investigation of the tubers of *D. polygonoides* has resulted in the isolation of a novel polyoxygenated spirostanol saponin, named diospolysaponin A (I), along with a known spirostanol saponin (prosapogenin A). The structure of I was determined on the basis of spectroscopic anal. and by enzymic hydrolysis followed by chromatog. and spectroscopic studies to be (23S,25R)-12α,14α,17α,23-tetrahydroxySpirost-5-ene-3β-yl O-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside. The cytotoxic activity of I and prosapogenin A and their aglycons against HSC-2 cells is briefly presented.

IT 623910-02-1P, Diospolysaponin A sapogenin 623939-65-1P, Diospolysaponin A
 RL: BSU (Biological study, unclassified); NPO (Natural product occurrence); PRP (Properties); PUR (Purification or recovery); BIOL (Biological study); OCCU (Occurrence); PREP (Preparation)
 (diospolysaponin A is a new polyoxygenated spirostanol saponin from the tubers of *Dioscorea polygonoides*)
 RN 623910-02-1 CAPLUS
 CN Spirost-5-ene-3,12,14,17,23-pentol, (3β,12α,23S,25R)-(9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

ACCESSION NUMBER: 2003:435935 CAPLUS

DOCUMENT NUMBER: 139:149817

TITLE: New Oxidative Tools for the Functionalization of the Cephalostatin North 1 Hemisphere Lee, Jong Seok; Fuchs, Philip L.

AUTHOR(S): Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA

CORPORATE SOURCE: Organic Letters (2003), 5(13), 2247-2250
 CODEN: ORLETF; ISSN: 1523-7060

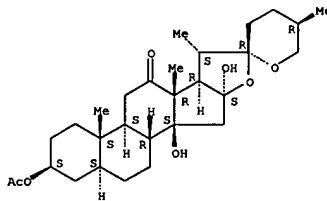
SOURCE: American Chemical Society

PUBLISHER: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 139:149817

GI



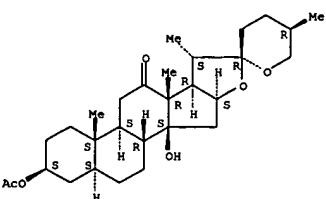
REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB New oxidative tools for the functionalization of the cephalostatin 1 northern hemisphere have been developed. Dimethylidioxirane (DMDO) C-H oxidation of ketone I ($\text{Y}=\beta\text{-OH}$, $\text{Z}=\text{H}$) to hemiketal I ($\text{Y}=\beta\text{-OH}$, $\text{Z}=\text{OH}$) (82%), bis-dehydration to vinyl ether II (77%), and DMDO again provides C-23 axial alc. III (99%). Routine processing, including a double-stereoselective Sharpless AD reaction ($\text{de} > 98\%$), gives alc. IV. Compound IV, bearing a C-23 silyl ether, undergoes Suarez hypoidide oxidative cyclization to generate unnatural spiroketal V.

IT 78216-38-3P 571185-76-7P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (new oxidative tools for the functionalization of the cephalostatin 1 northern hemisphere)
 RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3β,5α,14β,25R)-(9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-, (3β,5α,14β,25R)-(9CI) (CA INDEX NAME)

Absolute stereochemistry.

ACCESSION NUMBER: 2002:252611 CAPLUS

DOCUMENT NUMBER: 137:20507

TITLE: Cephalostatin Support Studies. 22. Dyotropic Rearrangement Facilitated Proximal Functionalization and Oxidative Removal of Angular Methyl Groups: Efficient Syntheses of 23'-Deoxy Cephalostatin 1 Analogues

AUTHOR(S): Li, Wei; LaCour, Thomas G.; Fuchs, P. L.
CORPORATE SOURCE: Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USASOURCE: Journal of the American Chemical Society (2002), 124(17), 4548-4549
CODEN: JACSAT; ISSN: 0002-7863

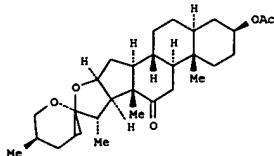
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 137:20507

GI



AB Oxidative functionalization (or removal) of a steroidial C18 Me group is possible using a previously unknown dyotropic rearrangement of a seven-membered fused C-ring lactone to a 6-ring spiro lactone.

Spiroketal equilibration led to the 23-deoxy South analog of cephalostatin 1 in only 12 steps (23% overall yield) from hecogenin acetate I, and to a strained diene South 1 analog in 11 steps (28% overall). Total synthesis of 23'-deoxy cephalostatin 1 was accomplished in 16 operations from I (9% overall; average 86% yield per operation), and that of 16',17'-dihydro-23'-deoxy cephalostatin 1 in 15 operations from I (8% overall; average 84% op).

IT 78216-38-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation of 23'-deoxycephalostatin 1 derivs. via dyotropic rearrangement)

RN 78216-38-3 CAPLUS
CN Spirostan-12-one, 3-(acetyloxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

ACCESSION NUMBER: 1999:270280 CAPLUS

DOCUMENT NUMBER: 131:45002

TITLE: A novel oxidative cleavage of the steroidal skeleton

AUTHOR(S): Jautelet, Rolf; Muller-Fahrnow, Anke; Winterfeldt, Ekkehard

CORPORATE SOURCE: Institut für Organische Chemie der Universität,

Hannover, D-30167, Germany

SOURCE: Chemistry - A European Journal (1999), 5(4), 1226-1233

PUBLISHER: Wiley-VCH Verlag GmbH

DOCUMENT TYPE: Journal

LANGUAGE: English

GI

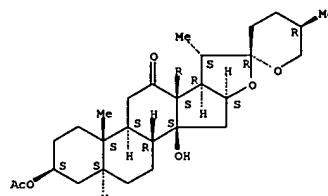
IT 434283-33-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of 23'-deoxycephalostatin 1 derivs. via dyotropic rearrangement)

RN 434283-33-7 CAPLUS

CN Spirostan-12-one, 3-(acetyloxy)-18-(formyloxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

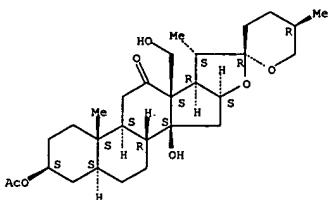
IT 434283-55-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of 23'-deoxycephalostatin 1 derivs. via dyotropic rearrangement)

RN 434283-55-3 CAPLUS

CN Spirostan-12-one, 3-(acetyloxy)-14,18-dihydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

(Continued)



REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

ACCESSION NUMBER: 1999:270280 CAPLUS

DOCUMENT NUMBER: 131:45002

TITLE: A novel oxidative cleavage of the steroidal skeleton

AUTHOR(S): Jautelet, Rolf; Müller-Fahrnow, Anke; Winterfeldt, Ekkehard

CORPORATE SOURCE: Institut für Organische Chemie der Universität,

Hannover, D-30167, Germany

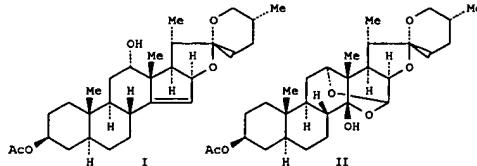
SOURCE: Chemistry - A European Journal (1999), 5(4), 1226-1233

PUBLISHER: Wiley-VCH Verlag GmbH

DOCUMENT TYPE: Journal

LANGUAGE: English

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AB With the objective of preparing higher oxygenated cephalostatin analogs and probing the importance of the $\Delta^{14,15}$ -double bond for biol. activity we investigated the syn-dihydroxylation of homomallylic alc. I. While this

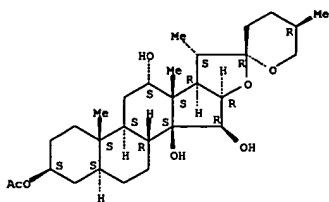
reaction took place with the expected β -diastereoselectivity using RuCl₃/NaIO₄ to provide the 14,15 β -glycol, we noticed that under more forcing conditions an oxidative cleavage occurred to yield the unusual bisketal II. This interesting transformation was applied to bissteroidal pyrazines to afford highly oxygenated cephalostatin analogs. Preliminary test results with these compds. indicated, however, a lack of cytostatic activity.

IT 227178-62-3P 227178-67-8P
RL: SPN (Synthetic preparation); PREP (Preparation)
(oxidative cleavage of the steroidal skeleton)

RN 227178-62-3 CAPLUS

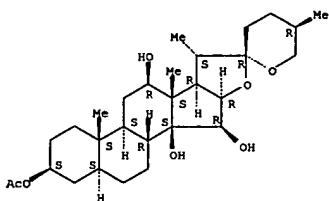
CN Spirostan-3,12,14,15-tetrol, 3-acetate, (3 β ,5 α ,12 α ,14,bet a,,15 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 227178-67-8 CAPLUS
CN Spirostan-3,12,14,15-tetrol, 3-acetate, (3β,5α,12β,14β)-
.15β,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



REFERENCE COUNT: 41 THERE ARE 41 CITED REFERENCES AVAILABLE FOR
THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE
FORMAT

ACCESSION NUMBER: 1998:69126 CAPLUS

DOCUMENT NUMBER: 128:115124

TITLE: Interphthal Product Splicing: The First Total Syntheses of Cephalostatin 1, the North Hemisphere of Ritterazine G, and the Highly Active Hybrid Analog, Ritterostatin GN1N

AUTHOR(S): LeClerc, Thomas G.; Guo, Chuangxing; Bhandaru, Sudhakar; Fuchs, P. L.; Boyd, Michael R.

CORPORATE SOURCE: Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA

SOURCE: Journal of the American Chemical Society (1998), 120(4), 692-707

CODEN: JACSAW; ISSN: 0002-7863

PUBLISHER: American Chemical Society

Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 128:115124

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Convergent total syntheses of the extremely potent cell growth inhibitor cephalostatin 1 and two hybrid analogs, ritterostatins GN1N (I) and GN1S (III), have been achieved. I is highly active in the 60 cell line human tumor panel of the National Cancer Institute. The North hemisphere of ritterazine G was efficiently constructed from hecogenin acetate in 15% yield over 13 steps. Extension of a key photolysis/Prins sequence to intermediates (III) and (IV) proceeded in excellent yield, leading to installation of the A14 moiety in the North G and South 1 steroid subunits as an application of a method for directed unsym. coupling of the

the cephalostatin and ritterazine components.

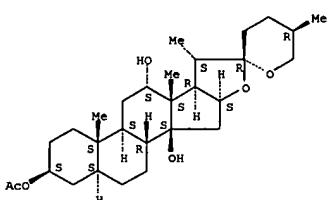
IT 78216-34-9P 78216-35-OP 78216-38-3P

RI: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(syntheses of cephalostatin 1, the north hemisphere of ritterazine G,
and the highly active hybrid analog, ritterostatin GN1N)

RN 78216-34-9 CAPLUS

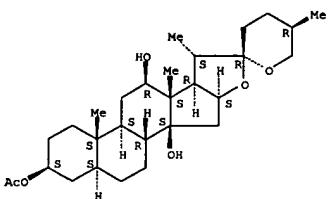
CN Spirostan-3,12,14-triol, 3-acetate, (3β,5α,12α,14β,2
5R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



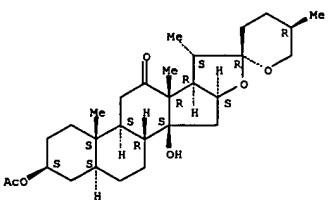
RN 78216-35-0 CAPLUS
CN Spirostan-3,12,14-triol, 3-acetate, (3β,5α,12β,14β,25
R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 78216-38-3 CAPLUS
CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3β,5α,14β,25
R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

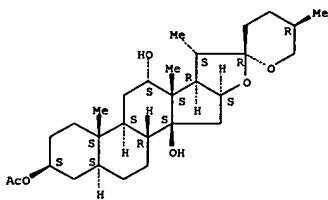


REFERENCE COUNT: 71 THERE ARE 71 CITED REFERENCES AVAILABLE FOR
THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE

FORMAT

L13 ANSWER 8 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1986:48145 CAPLUS
 DOCUMENT NUMBER: 104:48145
 TITLE: Carbon-13 NMR spectroscopy of steroid saponins
 and
 steroidal saponins
 AUTHOR(S): Agrawal, P. K.; Jain, D. C.; Gupta, R. K.; Thakur, R. S.
 CORPORATE SOURCE: Cent. Inst. Med. Aromat. Plants, Lucknow, 226016, India
 SOURCE: Phytochemistry (Elsevier) (1985), 24(11), 2479-96
 CODEN: PYTCAS; ISSN: 0031-9422
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB The 13C NMR chemical shifts of 130 naturally occurring steroid saponins and saponin derivs. published up to 1983 are listed and a number of methods for signal assignment are explained. The utility of 13C-NMR spectral anal. for the structure elucidation of these compds. is discussed.
 IT 78216-34-9 78216-35-0 78216-36-1
 78216-37-2 78216-38-3
 RL: PRP (Properties)
 (carbon-13 NMR chemical shifts of)
 RN 78216-34-9 CAPLUS
 CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



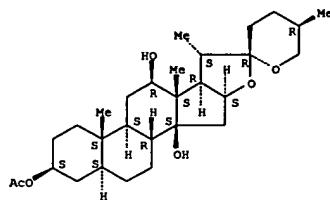
RN 78216-35-0 CAPLUS
 CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 β ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

RN 78216-37-2 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 β ,14 β ,25R)- (9CI) (CA INDEX NAME)

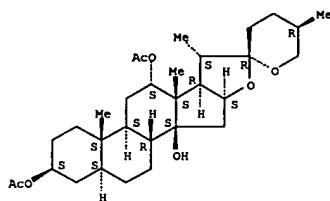
Absolute stereochemistry.

L13 ANSWER 8 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)



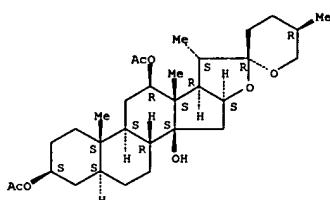
RN 78216-36-1 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 78216-37-2 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 β ,14 β ,25R)- (9CI) (CA INDEX NAME)

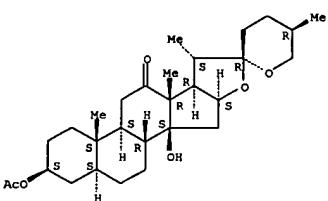
Absolute stereochemistry.



L13 ANSWER 8 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)

RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L13 ANSWER 9 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1983:135592 CAPLUS
 DOCUMENT NUMBER: 98:135592

TITLE: 14 β -Hydroxysteroid. VII. 14 β -Hydroxyhecogeninacetate, C29H44O6

AUTHOR(S): Paulus, E. F.
 CORPORATE SOURCE: Hoechst A.-G., Frankfurt/Main, 6230/80, Fed. Rep. Ger.

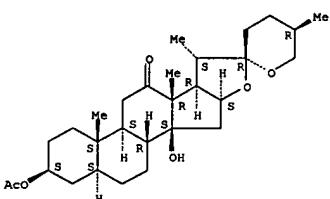
SOURCE: Acta Crystallographica, Section C: Crystal Structure Communications (1983), C39(3), 368-70
 CODEN: ACSCEE; ISSN: 0108-2701

DOCUMENT TYPE: Journal
 LANGUAGE: English

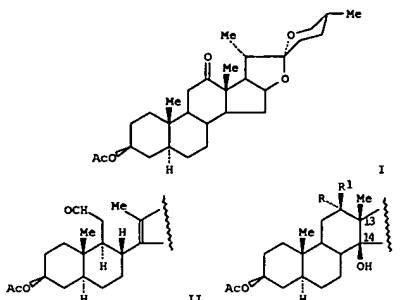
AB The title compound is monoclinic, space group P21, with a 13.248(10), b 6.762(7), c 16.09(4) Å, and β 108.9(1) $^\circ$; d_c = 1.190 and d_o = 1.16 for Z = 2. The structure was refined to a final R_w = 3.4% (1260 reflections). The 13 β -Me and 14 β -hydroxy configuration of the steroid was confirmed. Atomic coordinates are given.

IT 78216-38-3
 RL: PRP (Properties)
 (structure of)
 RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



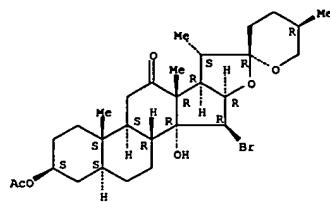
L13 ANSWER 10 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1981:443460 CAPLUS
 DOCUMENT NUMBER: 95:443460
 TITLE: 14β-Hydroxy steroids. II. Prins reaction of lumihecogenin acetate
 AUTHOR(S): Weizel, Peter; Janssen, Bernd; Duddeck, Helmut
 CORPORATE SOURCE: Abt. Chem., Univ. Bochum, Bochum, D-4630, Fed. Rep. Ger.
 SOURCE: Liebigs Annalen der Chemie (1981), (3), 546-64
 CODEN: LACHDL; ISSN: 0170-2041
 DOCUMENT TYPE: Journal
 LANGUAGE: German
 GI



AB Photolysis of hecogenin acetate (I) gave lumihecogenin acetate (II), which underwent intramol. Prins reaction to give spirostanediols III ($R = H$, $R_1 = HO$; $R = HO$, $R_1 = H$). Configurations of III at C-13 and C-14 were determined by chemical correlation and NMR and CD spectroscopy.
 IT 78179-70-1P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and cyclization of)
 RN 78179-70-1 CAPLUS
 CN Spirostan-3-one, 3-(acetyloxy)-15-bromo-14-hydroxy-, (3 β ,5 α ,15 β ,25R)- (9CI) (CA INDEX NAME)

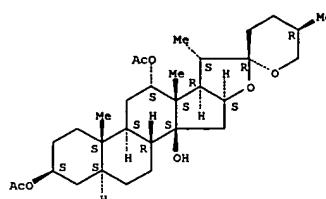
Absolute stereochemistry.

L13 ANSWER 10 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)



IT 78216-36-1P 78216-37-2P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and dehydration of)
 RN 78216-36-1 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

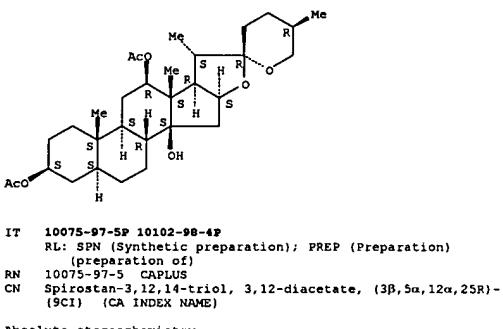
Absolute stereochemistry.



RN 78216-37-2 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 β ,14 β ,25R)- (9CI) (CA INDEX NAME)

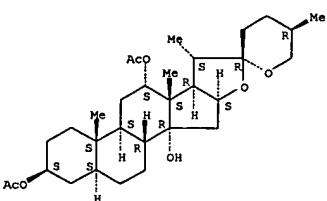
Absolute stereochemistry.

L13 ANSWER 10 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)



IT 10075-97-5P 10102-98-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 RN 10075-97-5 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 α ,25R)- (9CI) (CA INDEX NAME)

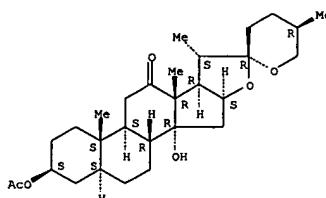
Absolute stereochemistry.



RN 10102-98-4 CAPLUS
 CN Spirostan-12-one, 3-(acetyloxy)-14-hydroxy-, (3 β ,5 α ,25R)- (9CI) (CA INDEX NAME)

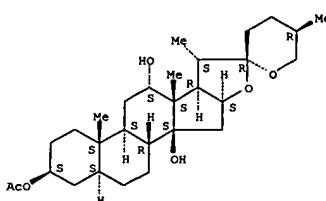
Absolute stereochemistry.

L13 ANSWER 10 OF 13 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)



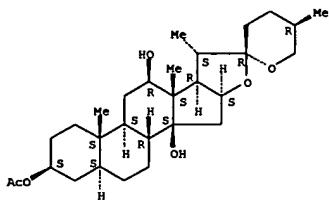
IT 78216-34-9P 78216-35-0P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of, by Prins reaction of lumihecogenin acetate)
 RN 78216-34-9 CAPLUS
 CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 78216-35-0 CAPLUS
 CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 β ,14 β ,25R)- (9CI) (CA INDEX NAME)

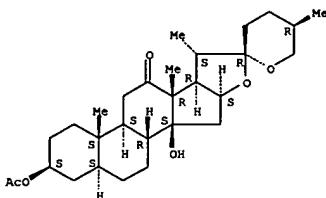
Absolute stereochemistry.



IT 78216-38-3
RL: RCT (Reactant); PACT (Reactant or reagent)
(reduction of)

RN 78216-38-3 CAPIUS
CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



ACCESSION NUMBER: 1967:85947 CAPIUS

DOCUMENT NUMBER: 66:85947

TITLE: Oxidation and solvolysis of lumi- and photohecogenin and their derivatives

AUTHOR(S): Chinn, Leland J.

CORPORATE SOURCE: G. D. Searle and Co., Chicago, IL, USA

JOURNAL: Journal of Organic Chemistry (1967), 32(3), 687-9

CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 66:85947

GI For diagram(s), see printed CA Issue.

AB Oxidation of either lumihecogenin (Ia) or photohecogenin with chromium trioxide in dilute acetic acid gives 14 α -hydroxyhecogenone (II). As solvolysis of lumihecogenin acetate (Ib) and photohecogenin acetate in dilute acetic acid affords 12 α ,14 α -dihydroxytigogenin 3-acetate, the mechanism of the oxidation of Ia is considered to be one

in which cyclization precedes oxidation to give the β -hydroxycyclohexanone system of II.

IT 10075-96-4P 10075-97-5P 10102-98-4P

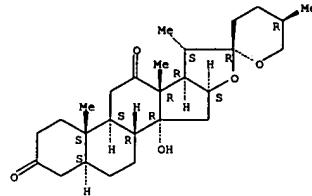
10102-99-5P

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 10075-96-4 CAPIUS

CN 5 α -Spirostan-3,12-dione, 14-hydroxy-, (25R)- (9CI) (CA INDEX NAME)

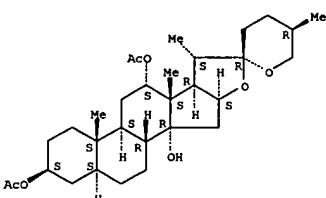
Absolute stereochemistry.



RN 10075-97-5 CAPIUS

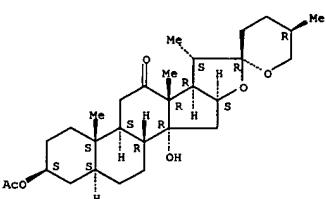
CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



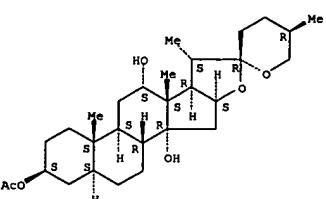
RN 10102-98-4 CAPIUS
CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 10102-99-5 CAPIUS
CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



ACCESSION NUMBER: 1964:20779 CAPLUS

DOCUMENT NUMBER: 60:20779

ORIGINAL REFERENCE NO.: 60:3654c-d

TITLE:

Steroids derived from hecogenin. III. The photochemistry of hecogenin acetate
 Bladon, Peter; McMeekin, William; Williams, Ivor A.
 Roy. Coll. Sci. Technol., Glasgow, UK
 Journal of the Chemical Society, Abstracts (1963),
 (Dec.), 5272-37
 CODEN: JCSAAZ; ISSN: 0590-9791

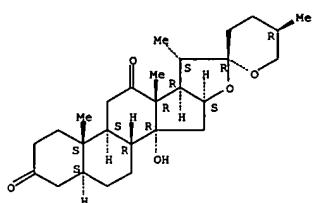
DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

OTHER SOURCE(S): CASREACT 60:20779

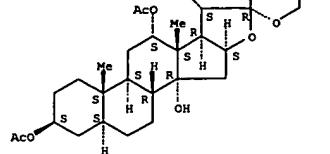
AB cf. CA 56, 4823f. Photolysis of hecogenin acetate yields
 3 β -acetoxy-12,13-seco-5 α ,25D-spirostan-13-en-12-one
 (lumhecogenin acetate) and 3 β -acetoxy-12 α ,14-epoxy-
 5 α ,25D-spirostan (photohecogenin acetate). The further
 transformation of these compds. into 14 α -hydroxyhecogenin and into
 14 α -unsubst. spirostan derivs. is also described.
 IT 10075-97-5 5 α ,25D-Spirostan-3,12-dione, 14-hydroxy-
 10075-97-5 5 α ,25D-Spirostan-3 β ,12 α ,14-triol,
 3,12-diacetate 10102-98-4, Hecogenin, 14-hydroxy-, 3-acetate
 10102-99-5 5 α ,25D-Spirostan-3 β ,12 α ,14-triol,
 3-acetate 107302-94-3, 5 α ,25D-Spirostan-12 α -
 carbonitrile, 3 β ,12,14-trihydroxy-, 3-acetate 107329-54-4,
 5 α ,25D-Spirostan-12-one, 3 β ,14-dihydroxy- 107330-69-8
 , 5 α ,25D-Spirostan-3 β ,12 α ,14-triol 108172-70-9,
 Hecogenin, 14-hydroxy-
 (preparation of)
 RN 10075-96-4 CAPLUS
 CN 5 α -Spirostan-3,12-dione, 14-hydroxy-, (25R)- (7CI) (CA INDEX NAME)

Absolute stereochemistry.



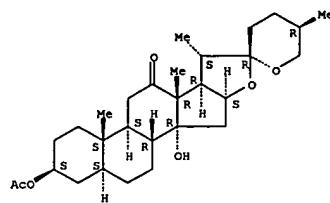
RN 10075-97-5 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 α ,25R)-
 (9CI) (CA INDEX NAME)

Absolute stereochemistry.



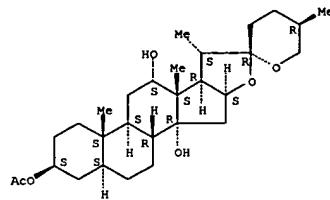
RN 10102-98-4 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



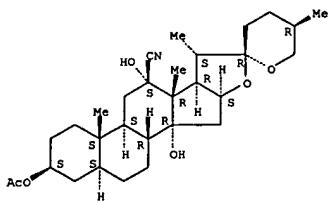
RN 10102-99-5 CAPLUS
 CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 α ,25R)-
 (9CI) (CA INDEX NAME)

Absolute stereochemistry.



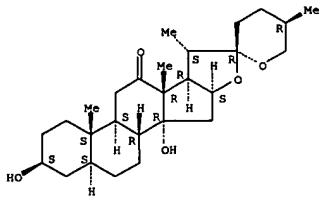
RN 107302-94-3 CAPLUS
 CN 5 α ,25D-Spirostan-12 α -carbonitrile, 3 β ,12,14-trihydroxy-,
 3-acetate (7CI) (CA INDEX NAME)

Absolute stereochemistry.



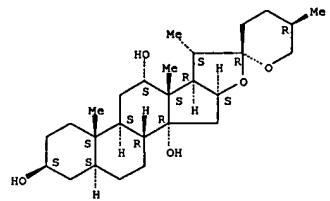
RN 107329-54-4 CAPLUS
 CN 5 α ,25D-Spirostan-12-one, 3 β ,14-dihydroxy- (7CI) (CA INDEX NAME)

Absolute stereochemistry.



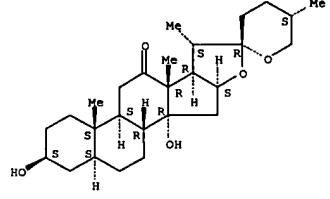
RN 107330-69-8 CAPLUS
 CN 5 α ,25D-Spirostan-3 β ,12 α ,14-triol (7CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 108172-70-9 CAPLUS
 CN Hecogenin, 14-hydroxy- (7CI) (CA INDEX NAME)

Absolute stereochemistry.



ACCESSION NUMBER: 1962:449520 CAPLUS

DOCUMENT NUMBER: 57:49520

ORIGINAL REFERENCE NO.: 57:99221, 9923a-b

TITLE: Photochemistry of hecogenin derivatives: a novel cyclization reaction of C-seco steroids

AUTHOR(S): Bladon, Peter; McMeekin, W.; Williams, Ivor A.

CORPORATE SOURCE: Roy. Coll. Sci. Technol., Glasgow, UK

SOURCE: Proc. Chem. Soc. (1962) 225-6

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

OTHER SOURCE(S): CASREACT 57:49520

A8 Ultraviolet irradiation of hecogenin acetate (I) in dioxane gave β -acetoxy-12-oxo-12,13-seco-5 α ,25D-spirostan-13-ene (II) (lumihecogenin acetate), confirmed by nuclear magnetic resonance identification of the aldehyde group. Reduction of II with LiAlH₄ gave anhydrohecetyl alcohol (III). Oxidation of II with CrO₃ in aqueous H₂SO₄-acetone

gave 14 α -hydroxyhecogenin acetate (IV). Conversion of IV to β -acetoxy-14 α -hydroxy-5 α -pregn-16-ene-12,20-dione confirmed the hydroxyl group at position 14. These reactions showed the double bond in III to be in the 13-position.

IT 10102-98-4, Hecogenin, 14-hydroxy-, acetate

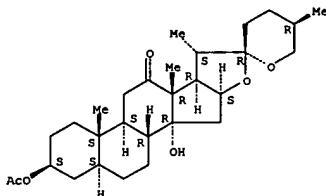
(preparation of)

RN 10102-98-4 CAPLUS

CN Spirostan-12-one, 3-(acetyloxy)-14-hydroxy-, (3 β ,5 α ,25R)- (9CI)

(CA INDEX NAME)

Absolute stereochemistry.



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NEWS 10 JAN 13 New IPC 8 SEARCH, DISPLAY, and SELECT enhancements added to
INPADOC
NEWS 11 JAN 17 Pre-1988 INPI data added to MARPAT
NEWS 12 JAN 17 IPC 8 in the WPI family of databases including WPIFV

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      24307 OXIDIZE
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L1      32965 OXIDIZE
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=> s 11 and hemiacetal
3691 HEMIACETAL
1145 HEMIACETALS
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L2 20 L1 AND HEMIACETAL

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L5 1290 L4 AND OXIDANT

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L6 3 L5 AND HEMIACETAL

=> d 16 1-3

L6 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2004:372938 CAPLUS
DN 140:391402
TI Catalytic oxidation of C-H bonds and its application to
α-hydroxylation of cyclic steroidal ethers
IN Fuchs, Philip; Lee, Seongmin
PA USA
SO U.S. Pat. Appl. Publ., 38 pp.
CODEN: USXXCO
DT Patent
LA English
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----------------------|----------|------------|-----------------|----------|
| PI US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |
| PRAI US 2002-403498P | P | 20020814 | | |
| OS | CASREACT | 140:391402 | | |

L6 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
AN 1962:73602 CAPLUS
DN 56:73602
OREF 56:14332e-i,14333a-i,14334a-i,14335a-i,14336a
TI Diterpenoid bitter principles. III. Constitution of clerodin
AU Barton, D. H. R.; Cheung, H. T.; Gross, A. D.; Jackman, L. M.;
Martin-Smith, M.
CS Imp. Coll., London
SO Journal of the Chemical Society, Abstracts (1961) 5061-73
CODEN: JCSAAZ; ISSN: 0590-9791
DT Journal
LA Unavailable

L6 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
AN 1958:113234 CAPLUS
DN 52:113234
OREF 52:19958f-i,19959a-f
TI Hydrogenolysis of carbohydrates. IV. 1,2-O-Isopropylidene-D-glucofuranose
AU Goto, P. A. J.; Perlin, A. S.
CS Natl. Research Council Can., Saskatoon
SO Canadian Journal of Chemistry (1958), 36, 661-6
CODEN: CJCAGG; ISSN: 0008-4042
DT Journal
LA English

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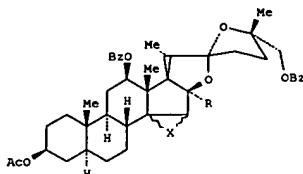
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L7 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:37293B CAPLUS
 DOCUMENT NUMBER: 140:391402
 TITLE: Catalytic oxidation of C-H bonds and its application
 to α -hydroxylation of cyclic steroidal ethers
 INVENTOR(S): Fuchs, Philip; Lee, Seongmin
 PATENT ASSIGNEE(S): USA
 SOURCE: U.S. Pat. Appl. Publ., 38 pp.
 CODEN: USXXCO
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---------------|------|----------|-----------------|----------|
| US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |

<-- PRIORITY APPLN. INFO.: US 2002-403498P P 20020814

OTHER SOURCE(S): CASREACT 140:391402
 GI



I

AB The invention provides a catalytic, chemospecific and stereospecific method of oxidizing a wide variety of substrates without unwanted side reactions. Essentially, the method of the instant invention, under relatively mild reaction conditions, catalytically, stereospecifically and chemospecifically inserts oxygen into a hydrocarbon C-H bond. Oxidation (oxygen insertion) at a tertiary C-H bond to form an alc. (and in some cases a hemiacetal) at the tertiary carbon is favored. The stereochemistry of an oxidized tertiary carbon is preserved. Ketones are formed by oxidizing a secondary C-H bond and ring-cleaved diones are formed by oxidizing cis tertiary CH bonds. Thus, epoxycalc. I ($X = O$, $R = OH$) was prepared by reacting spiroketal compound I ($X = \text{bond}$, $R = H$) in an anhydrous solvent with chromium [VI] oxidant and a co-oxidant at a reaction temperature between about -100° C to about 0° C and a reaction time of between about 30 min to about 3 h. The method is useful in the synthesis of intermediates appropriate for preparation of analogs of the cephalostatin/ritterazine family of marine natural products.

L7 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)

```
=> s oxidation
    426097 OXIDATION
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        (OXIDATION OR OXIDATIONS)
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L8      867233 OXIDATION
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=> s 18 and chromium
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L11     6 L10 AND STEROID

=> d ibib abs 1-6
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L11 ANSWER 1 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:896751 CAPLUS

DOCUMENT NUMBER: 141:332365

TITLE: An improved process for the production of 17-keto
steroids from 20-keto steroids

INVENTOR(S): Borah, Parinita; Chowdhury, Prithish Kumar; Ghosh,

Anil

C.

PATENT ASSIGNEE(S): Council of Scientific & Industrial Research, India
SOURCE: Indian, 31 pp.

CODEN: INXXAP

DOCUMENT TYPE: Patent

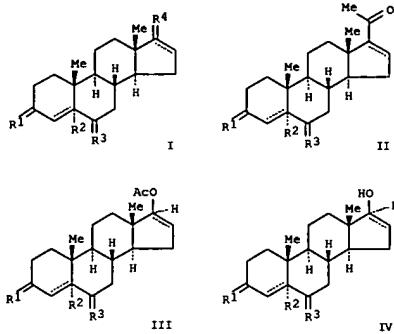
LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|-----------------------|------|----------|-----------------|----------|
| IN 184308 | A | 20000805 | IN 1995-DE2465 | 19951229 |
| PRIORITY APPN. INFO.: | | | IN 1995-DE2465 | 19951229 |

OTHER SOURCE(S): CASREACT 141:332365; MARPAT 141:332365
GI



AB An improved process for the preparation of 17-ketosteroids I [Δ^3 (sic), R₁ = R₄ = O, R₃ = H₂; R₁ = R₄ = O, R₂ = Br, Cl, R₃ = (Br, α -H); Δ^3 (sic), R₁ = R₃ = R₄ = O] comprising following steps: (1) oxidizing 20-ketosteroids II [Δ^3 (sic), R₁ = O, R₃ = H₂; R₁ = O, R₂ = H, R₃ = H₂; R₁ = (β -OAc, α -H), R₂ = H, R₃ = H₂; R₁ = (Br-OAc, α -H), R₂ = Br, Cl, R₃ = (Br, α -H), Δ^3 (sic), Δ^{16} , R₁ = R₃ =

L11 ANSWER 2 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1988:590662 CAPLUS

DOCUMENT NUMBER: 109:190662

TITLE: New developments in the chemistry of peroxy-metal and chromium(VI)-oxidant systems

AUTHOR(S): Chaudhuri, Mihir K.
CORPORATE SOURCE: Dep. Chem., North-Eastern Hill Univ., Shillong,
793003, India

SOURCE: Journal of Molecular Catalysis (1988), 44(1), 129-41
CODEN: JMCAFD; ISSN: 0304-5102

DOCUMENT TYPE: Journal; General Review

LANGUAGE: English

AB The importance of syntheses and studies of reactivity of peroxy-metal compds., which provide a heuristic approach in this field for an understanding of catalytic oxidation reactions, has been highlighted. Innovative approaches and their scope in the synthesis of new heteroligand peroxymetal compds. are described. The metals are drawn from Ti, Zr, V, Cu and U; heteroligands include F-, Cl-, SO₄²⁻, CO₃²⁻, ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline and glycine. Various reactions of some of these compds. are summarized. The oxidants of organic substrates involving a new Cr(VI) reagent, pyridine fluorochromate, C₅H₅NHC₂O₃F (PFC), are described. PFC in dichloromethane oxidizes primary and secondary alics. to the corresponding aldehydes and ketones, benzoin and a tricyclic allylic alc. to benzil and a tricyclic enone, and anthracene and phenanthrene to anthraquinone and phenanthrene-9,10-quinone, resp. Selective oxidation of secondary alics. in the presence of primary ones, including that of 5-androstan-3B,17B-diol to the 17-keto steroid, by PFC is another significant feature of the oxidant. The oxidation of PPh₃ to OPPh₃ provides a clear-cut example of an oxygen transfer reaction involving the PFC system. Synthetic utility of the new reagent is accentuated. A review with 62 refs.

L11 ANSWER 1 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)
by selective Baeyer-Villiger oxida. process using peracids in the presence of a Lewis acid in an org. solvent at a temp. 0 to 30°C, to obtain 17-acetoxysteroids III; (2) mild alk. hydrolysis of the 17-acetoxysteroids III to produce 17-hydroxysteroids IV; and (3) oxidizing the resultant 17-hydroxysteroids IV using conventional oxidant to produce the 17-ketosteroids. Thus, I [R₁ = R₄ = O, R₂ = H, R₃ = H₂] was prep'd. from II [R₁ = β -OAc, R₂ = H, R₃ = H₂] via Baeyer-Villiger oxida. with PhCO₃H in CH₂Cl₂ contg. catalytic SnCl₄, hydrolysis with NaOH in aq. EtOH, and oxida. of, with pyridinium chlorochromate.

L11 ANSWER 3 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1979:541068 CAPLUS

DOCUMENT NUMBER: 91:141068

TITLE: Preparation of Δ^5 -7-oxo steroids by allylic oxidation of Δ^5 sterols: a study of the reactivity of the chromium trioxide-pyridine 1:1 and 1:2 complexes prepared in situ

AUTHOR(S): Mappas, Elisabeth; Cuilleron, Claude Yves
CORPORATE SOURCE: Unite Rech. Endocrinogenes Metab. Enfant, Hop.
Debroussse, Lyon, Fr.

SOURCE: Journal of Chemical Research, Synopses (1979), (2), 42-3
CODEN: JRPSDC; ISSN: 0308-2342

DOCUMENT TYPE: Journal

LANGUAGE: English/French

AB Allylic oxidns. of protected Δ^5 sterols to Δ^5 7-oxo sterols were carried out with CrO₃-pyridine 1:1 and 1:2 complexes prepared in situ in CH₂Cl₂. The 1:1 complex reacts more

rapidly than the 1:2 complex. The reaction rate increases on using a 25-fold excess of either complex, by preparing the oxidants in the presence of P2O₅, and by raising the temperature to 41°. The Δ^5 7-ketones were obtained in comparable yields (generally 50-90%) with either complex. The oxidation of 3 β -hydroxy- Δ^5 sterols and Δ^5 steroid 3-ethyleneacetals is also reported. The relative stability of acetate, ethyleneacetal, and tetrahydropyran protecting groups in CrO₃-pyridine allylic oxidns. was examined. 20-Ethyleneacetals and Δ^4 - and Δ^4 ,6-3-ethyleneacetals were converted to the corresponding ketones despite the basic anhydrous medium.

L11 ANSWER 4 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1977:601877 CAPLUS
 DOCUMENT NUMBER: 87:201877
 TITLE: Oxidation with chromium(VI)
 oxide-pyridine complex. A study of reaction
 parameters using cholesterol as substrate
 AUTHOR(S): Piers, Edward; Worster, Paul M.
 CORPORATE SOURCE: Dep. Chem., Univ. British Columbia, Vancouver, BC,
 Can.
 SOURCE: Canadian Journal of Chemistry (1977), 55(4), 733-6
 CODEN: CJCHAG; ISSN: 0008-4042
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB Oxid. of cholesterol (I) with CrO₃-pyridine complex under various
 conditions produced cholest-5-en-3-one (II) accompanied by varying amounts
 of cholest-4-ene-3,6-dione. The efficiency of the oxidation and
 the product distribution were dependent on the atmospheric, temperature,
 molar ratio of
 oxidant to substrate, molar ratio of pyridine to CrO₃, the
 heterocyclic amine used, and the proton source employed. The yield of II
 was optimized by oxidation of I with a 10-fold excess of the
 monopyridine-CrO₃ complex in CH₂Cl₂ under a N atmospheric at 0°C.

L11 ANSWER 5 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1957:47110 CAPLUS
 DOCUMENT NUMBER: 51:47110
 ORIGINAL REFERENCE NO.: 51:8772g-i
 TITLE: Steroids. XXVII. The oxidation of
 5-cholest-3B-ol with chromium
 trioxide
 AUTHOR(S): Kucera, J.; Jirat, E.; Schwarz, V.
 CORPORATE SOURCE: Chem. ustav CSAV, Prague
 SOURCE: Cesko-Slovenska Farmacie (1956), 5, 331-5
 CODEN: CKFRAY; ISSN: 0009-0530
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 AB cf. C.A. 51, 1234f. The conditions for the oxidation of
 5-cholest-3B-ol (I) to 3-hydroxy-17-oxo-5-androstan-17-one (II) and
 3-hydroxy-5-cholenic acid (III) were studied. I (27.8 g.) in 200 ml.
 (CH₂Cl)₂ was treated, with stirring and ice cooling with 11.4 g. Br in
 135 ml. (CH₂Cl)₂, kept overnight, diluted with 290 ml. AcOH, cooled and
 stirred, while the oxidant (65 g. CrO₃, 83 ml. H₂O, 300 ml. AcOH, and 100
 g. concentrated H₂SO₄) was gradually added within 1 hr., with the
 temperature kept at
 21°, the solution stirred 22 hrs., the excess CrO₃ reduced with MeOH,
 the steroids were debrminated with 20 g. Zn in AcOH, the acid
 separated from the neutral products by extraction with 20% NaOH, the
 neutral fraction was isolated in the form of the acetates, and the acid fraction
 after deacetylation, in the form of the free acids. In this procedure
 were varied the temperature (0-20-50°), amounts of CrO₃ (50-100-200%), H₂O
 (50-100-200%), and H₂SO₄ (50-100-200%), and the solvents CC₁₄ or
 (CH₂Cl)₂.
 Increasing temperature, CrO₃ concentration, and especially H₂SO₄
 concentration, increased,
 whereas H₂O and CC₁₄ decreased the velocity of oxidation. With
 higher concns. of H₂SO₄ the yield of II increased, and that of III
 decreased. The reaction products were followed by semiquant. paper
 chromatography.

L11 ANSWER 6 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1957:9688 CAPLUS
 DOCUMENT NUMBER: 51:9688
 ORIGINAL REFERENCE NO.: 51:2073d-1,2074a-f
 TITLE: Oxidation of steroid enamines
 INVENTOR(S): Holysz, Roman F.; Babcock, John C.
 PATENT ASSIGNEE(S): Upjohn Co.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|----------|-------|-----------------|-------|
| ----- | ----- | ----- | ----- | ----- |
| US 2752369 | 19560626 | US | | |

 AB Physiologically and therapeutically active 20-oxo steroids are produced by the oxidation of 22-(tertiary amino)-Δ20(22)-steroids by CrO₃-heterocyclic amine complexes. (COC₁₂) (10 ml.) in C₆H₆ and 3.3 g. 3,11-dioxo-5-bisnorcholenic acid were refluxed 30 min. in the presence of pyridine and distilled to eliminate excess (COC₁₂), yielding 3,11-dioxo-4-bisnorcholenyl chloride (I). The cold crude I in 100 ml. C₆H₆ was heated 10 min. on the steam bath with 4.5 ml. PhNHMe, cooled, washed to neutrality to phenolphthalein with 3 portions of 5 ml. H₂O, 15 ml. 5% HCl, 15 ml. 5% NaOH, and several 5 ml. portions H₂O. The dried solution was evaporated and the residue recrystd. from MeOH and H₂O to give the methylanilide (Ia). Ia, 3 ml. distilled HOCH₂CH₂OH, 150 mg. p-MeC₆H₄SO₃H, and 60 ml. C₆H₆ were refluxed 10 hrs. with stirring, cooled, washed with dilute NaHCO₃ and H₂O, dried, and evaporated in vacuo to give colorless crystalline 3,11-dioxo-5-bisnorcholenic acid methylanilide 3-ethylene ketal (II) (from EtOAc-Skellysolve). II in 30 ml. tetrahydrofuran was added dropwise to 1.2 g. LiAlH₄ in 100 ml. anhydrous Et₂O, stirred 30 min. at 0-5° and 1 hr. at 25°, refluxed 1 hr., cooled, hydrolyzed with 15 ml. H₂O, and decanted. The pasty residue was suspended in H₂O and extracted with CH₂Cl₂. Evaporation of the combined exts. and organic layer gave quantitatively crystalline 11B-hydroxy-3-oxo-5-bisnorcholen-22-ol 3-ethylene ketal, converted in 30 ml. AcOH by standing overnight at 22-25° with 5 ml. Ac₂O and 0.3 g. p-MeC₆H₄SO₃H to the corresponding 11B-acetate (III). III (2.25 g.) in 50 ml. C₆H₆ containing 2 ml. piperidine was refluxed 2 hrs. in a N atmospheric with return of the condensate through 8 g. Al₂O₃. The C₆H₆ was distilled in vacuo and the residue taken up in 10 ml. MeOH, cooled to 4°-3.5 hrs., and filtered. The residue was washed with 1 ml. cold MeOH to give 11B-acetoxy-22-piperidino-5,20(22)-bisnorcholadien-3-one 3-ethylene ketal (IV). Similarly, 3-oxo-4-bisnorcholenic acid, a hitherto discarded by-product in the synthesis of progesterone from stigmasterol, is converted to IV. In the same manner, bisnordeoxycholic acid was converted to the 3a,12a-diester, transformed by treatment with SOCl₂ and PhNHMe followed by reduction with LiAlH₄ to 3a,12a-dihydroxy-22-morpholinio-20(22)-bisnorcholen (V), yielding 3a,12a-dihydroxy-22-morpholinio-20(22)-bisnorcholen (VI) on heating with morpholine. V (1 g.) in 3 ml. pyridine and 1 ml. Ac₂O was kept 2 hrs. at room temperature, poured

L11 ANSWER 6 OF 6 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)
 into 50 ml. cracked ice and H₂O, and filtered. Crystrn. of the residue gave pure 3a,12a-diacetoxylbisnorcholan-22-ol, converted by heating with morpholine to 3a,12a-diacetoxyl-22-morpholinio-20(22)-bisnorcholen (VII). Treatment of 1 g. 11a,22-dihydroxy-3-oxo-4-bisnorcholen in 5 ml. pyridine with 0.5 ml. MeCC₁₄ 6 hrs. at room temp., pouring into H₂O, extg. with CH₂Cl₂, washing the exts. with dil. acetic acid and H₂O, drying and evapd. gave crude 11a-hydroxy-22-trimethylacetoxyl-3-oxo-4-bisnorcholen. The crude material in 5 ml. pyridine was refrigerated 16 hrs. with 0.5 g. p-MeC₆H₄SO₃H, warmed to room temp. and poured into 100 ml. H₂O. The dried ppt. in 5 ml. AcOH was refluxed 4 hrs. with 0.5 g. KOAc, poured into H₂O, and the dried washed product in 0.3 g. NaOH in 5 ml. EtOH was kept 2 hrs. at room temp., dill. with 50 ml. C₆H₆, neutralized with dil. HCl, and filtered. Crystrn. from MeOH gave 22-hydroxy-3-oxo-4,9(11)-bisnorcholadiene (VIII). VIII in 50 ml. C₆H₆ (dried over Na and 2 g. quinone) was refluxed 18 hrs. with 1 g. Al(iso-Pro)₃, cooled, dill. with 25% H₂SO₄ and extd. with CH₂Cl₂ to give 3-oxo-4,9(11)-bisnorcholadien-22-ol (IX) (from MeOH). IX in 20 ml. C₆H₆ and 1 ml. piperidine was refluxed 2 hrs., under N, in vacuo and the residue taken up in 3 ml. MeOH. The ext. was cooled 4 hrs. at 0° and filtered. The residue was washed with H₂O and cold dil. MeOH, and dried yielding 3-oxo-22-piperidino-4,9(11),20(22)-bisnorcholatriene (X). A stirred suspension of 6 g. CrO₃ in 60 ml. pyridine was treated in 1 hr. at 5-10° with 11.87 g. 22-piperidino-4,20(22)-bisnorcholadien-3-one (XI) in 90 ml. pyridine, stirred 2 hrs. at 8-10° and 15 hrs. at 10-20°, poured into 200 ml. concd. HCl and 200 g. crushed ice, and shaken with 100 ml. C₆H₆ and 25 g. NaHSO₃. The green aq. layer was twice extd. and washed with 50 ml. 10% HCl, 50 ml. H₂O, two 50-ml. portions 10% NaOH, 50 ml. H₂O, 50 ml. 10% HCl, and two 50-ml. portions H₂O. The soln. was filtered and evapd. in vacuo yielding 6.7 g. crude material, to give 3.83 g. progesterone, m. 127-9°. In the same manner, progesterone is produced by treating pyrrolidyl, morpholinio, dibenzylamino, dimethylamino, diethylamino, dibutylamino, dicyclohexylamino, tetrahydroquinolinyl, diocetylaminio, oxazolidinyl, N-methylamino, N-methyltoluidinyl, N-methylanisidinyl, diethanolamino, methylbenzylamino, and other like 22-(tertiary amino)-4,20(22)-bisnorcholadien-3-ones with pyridine, quinoline, or other heterocyclic amine-CrO₃ complexes. Similarly, oxidation of 22-piperidino-4,20(22)-bisnorcholadiene-3,11-dione gave 11-oxo-progesterone. Oxidation of IV produced 11B-acetoxyprogesterone 3-ethylene ketal, hydrolyzed with HCl to 11B-acetoxyprogesterone. VI and VII were similarly oxidized to give pregnane-3,12,20-trione and 3a,12a-diacetoxypregnane-20-one. In the same manner 3B-acetoxy-22-piperidino-5,20(22)-bisnorcholadiene was oxidized with CrO₃ in a-picoline to give pregnenolone acetate and 3-acetoxy-22-N-pyrrolidyl-5,20(22)-bisnorcholatriene 5,8-maleic anhydride was oxidized with CrO₃ in β -picoline to give 3-acetoxy-5,7-pregnadien-20-one maleic anhydride adduct. X was selectively oxidized with CrO₃ in pyridine to yield 9(11)-dehydropregesterone.

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|--|------------|---------|
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| | ENTRY | SESSION |
| FULL ESTIMATED COST | 46.35 | 46.56 |
| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | SINCE FILE | TOTAL |
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| CA SUBSCRIBER PRICE | -5.25 | -5.25 |

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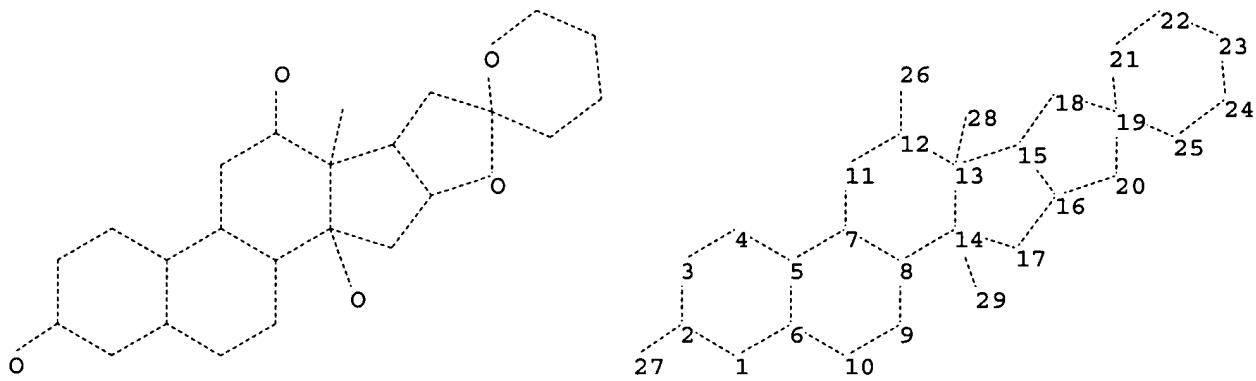
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DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

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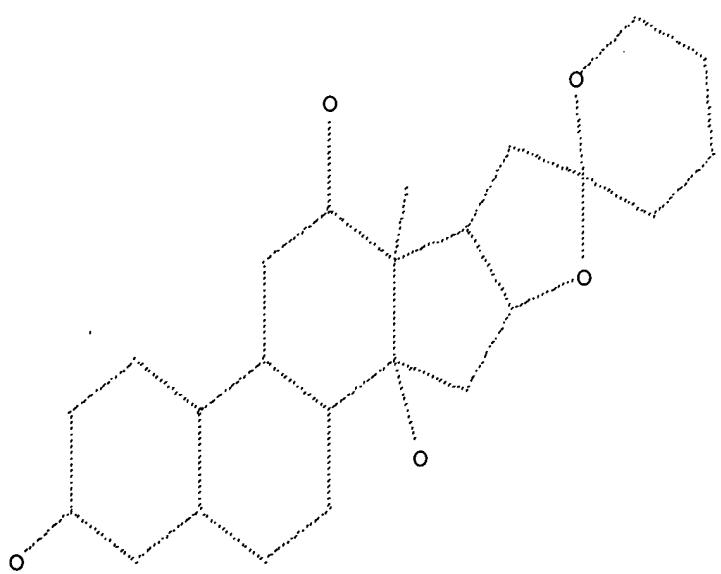
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* The CA roles and document type information have been removed from *
* the TDR default display format and the ED field has been added. *



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ring nodes :
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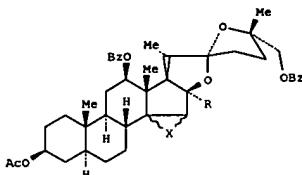
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74 CHROMIUMS
353370 CHROMIUM
(CHROMIUM OR CHROMIUMS)

L16 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:372938 CAPLUS
 DOCUMENT NUMBER: 140:391402
 TITLE: Catalytic oxidation of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers
 INVENTOR(S): Fuchs, Philip; Lee, Seongmin
 PATENT ASSIGNEE(S): USA
 SOURCE: U.S. Pat. Appl. Publ., 38 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM.: COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|------|----------|-----------------|------------|
| US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |
| PRIORITY APPLN. INFO.: | | | US 2002-403498P | P 20020814 |

OTHER SOURCE(S): CASREACT 140:391402
 GI



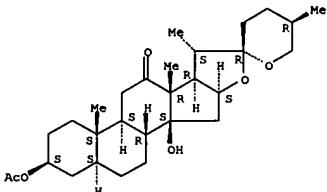
AB The invention provides a catalytic, chemospecific and stereospecific method of oxidizing a wide variety of substrates without unwanted side reactions. Essentially, the method of the instant invention, under relatively mild reaction conditions, catalytically, stereospecifically and chemospecifically inserts oxygen into a hydrocarbon C-H bond. Oxidation (oxygen insertion) at a tertiary C-H bond to form an alc. (and in some cases a hemiacetal) at the tertiary carbon is favored. The stereochemistry of an oxidized tertiary carbon is preserved. Ketones are formed by oxidizing a secondary C-H bond and ring-cleaved dienes are formed by oxidizing tertiary CH bonds. Thus, epoxycalc. I ($X = O$, $R = OH$) was prepared by reacting spiroketal compound I ($X = bond$, $R = H$) in an anhydrous solvent with chromium [VI] oxidant and a co-oxidant at a reaction temperature between about -100° C to about 0° C and a reaction time of between about 30 min to about 3 h. The method is useful in the synthesis of intermediates appropriate for preparation of analogs of the cephalostatin/ritterazine family of marine natural products.

IT 571185-76-7P
 RL: IMP (Industrial manufacture); SPN (Synthetic preparation); PREP

L16 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:261227 CAPLUS
 DOCUMENT NUMBER: 140:423861
 TITLE: An Efficient C-H Oxidation Protocol for α -Hydroxylation of Cyclic Steroidal Ethers
 AUTHOR(S): Lee, Seongmin; Fuchs, Philip L.
 CORPORATE SOURCE: Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA
 SOURCE: Organic Letters (2004), 6(9), 1437-1440
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 140:423861
 AB Various C-16 hydroxy steroids have been prepared with the aid of CrO_3/Bu_4NIO_4 . Out of the two possible reaction courses, transition state B is favored because of less steric interference between substrate and CrO_4 . Thus, C-H bonds at C-16 are oxidized selectively.

IT 78216-38-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (regio-, stereo- and chemoselective α -hydroxylation of cyclic steroidal ethers using CrO_3/Bu_4NIO_4)
 RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



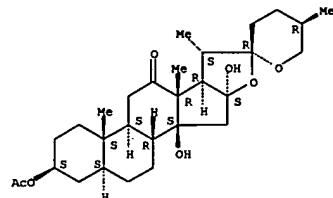
IT 571185-76-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (regio-, stereo- and chemoselective α -hydroxylation of cyclic steroidal ethers using CrO_3/Bu_4NIO_4)
 RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

L16 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)

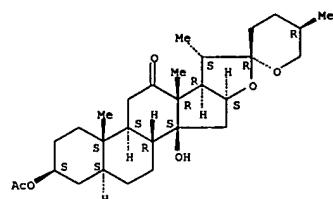
(Preparation)
 (catalytic oxida. of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers)
 RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 78216-38-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (catalytic oxidation of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers)
 RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L16 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)

REFERENCE COUNT: 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

IT 78216-38-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (regio-, stereo- and chemoselective α -hydroxylation of cyclic steroidal ethers using CrO_3/Bu_4NIO_4)
 RN 78216-38-3 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



ACCESSION NUMBER: 1967:85947 CAPLUS
 DOCUMENT NUMBER: 66:85947
 TITLE: Oxidation and solvolysis of lumi- and photohecogenin and their derivatives
 AUTHOR(S): Chin, Leland J.
 CORPORATE SOURCE: G. D. Searle and Co., Chicago, IL, USA
 SOURCE: Journal of Organic Chemistry (1967), 32(3), 687-9
 CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 66:85947

GI For diagram(s), see printed CA Issue.
 AB Oxidation of either lumihecogenin (Ia) or photohecogenin with chromium trioxide in dilute acetic acid gives 14 α -hydroxyhecogenone (II). As solvolysis of lumihecogenin acetate (Ib) and photohecogenin acetate in dilute acetic acid affords 12 α ,14 α -dihydroxytigogenin 3-acetate, the mechanism of the oxidation of Ia is considered to be one in which cyclization precedes oxidation to give the β -hydroxycyclohexanone system of II.

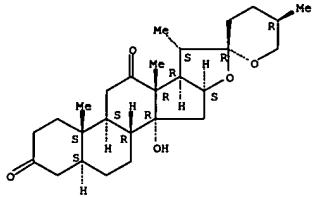
IT 10075-96-4P 10075-97-5P 10102-98-4P

10102-99-5P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)

RN 10075-96-4 CAPLUS

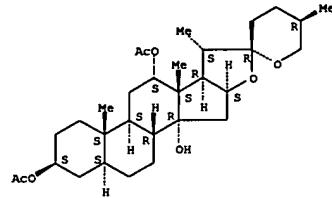
CN 5 α -Spirostan-3,12-dione, 14-hydroxy-, (25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



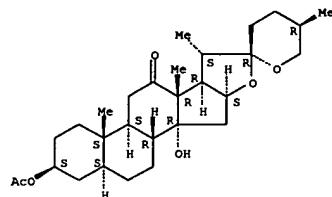
RN 10075-97-5 CAPLUS
 CN Spirostan-3,12,14-triol, 3,12-diacetate, (3 β ,5 α ,12 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



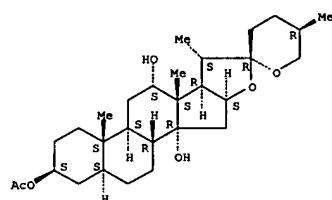
RN 10102-98-4 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14-hydroxy-, (3 β ,5 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 10102-99-5 CAPLUS
 CN Spirostan-3,12,14-triol, 3-acetate, (3 β ,5 α ,12 α ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



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  0 CHROMOYL
  0 DIACETATE
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=> s catalytic chromoyl diacetate
398529 CATALYTIC
26 CATALYTICS
398538 CATALYTIC
(CATALYTIC OR CATALYTICS)
2 CHROMOYL
38732 DIACETATE
1884 DIACETATES
39549 DIACETATE
(DIACETATE OR DIACETATES)
L19 1 CATALYTIC CHROMOYL DIACETATE
(CATALYTIC (W) CHROMOYL (W) DIACETATE)

=> d

L19 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2002:835050 CAPLUS
DN 138:72824
TI Cephalostatin Support Studies. 23. Chemospecific Chromium(VI) Catalyzed
Oxidation of C-H Bonds at -40°
AU Lee, Seongmin; Fuchs, P. L.
CS Department of Chemistry, Purdue University, West Lafayette, IN, 47907,
USA
SO Journal of the American Chemical Society (2002), 124(47), 13978-13979
CODEN: JACSAU; ISSN: 0002-7863
PB American Chemical Society
DT Journal
LA English
OS CASREACT 138:72824
RE.CNT 33 THERE ARE 33 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

| | | | |
|--|------|------------|---------|
| => FIL STNGUIDE | | SINCE FILE | TOTAL |
| COST IN U.S. DOLLARS | | ENTRY | SESSION |
| FULL ESTIMATED COST | 7.45 | | 239.75 |
| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | | SINCE FILE | TOTAL |
| CA SUBSCRIBER PRICE | 0.00 | ENTRY | SESSION |
| | | | -7.50 |

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 AND TECHNOLOGY CORPORATION, AND FACHINFORMATIONSZENTRUM KARLSRUHE

FILE CONTAINS CURRENT INFORMATION.
 LAST RELOADED: Jan 13, 2006 (20060113/UP).

=> s hydroxylateion
 0 HYDROXYLATEION
 L20 0 HYDROXYLATEION

=> s hydroxylation
 0 HYDROXYLATION
 L21 0 HYDROXYLATION

=> s oxidiz?
 L22 0 OXIDIZ?

=> s oxidiz
 => s oxidiz
 0 OXIDIZ
 L23 0 OXIDIZ

=> s oxidiz?
 L24 0 OXIDIZ?

=> s (oxidize or oxidizing or oxidation)
 0 OXIDIZE
 0 OXIDIZING
 3 OXIDATION
 L25 3 (OXIDIZE OR OXIDIZING OR OXIDATION)

| | | | |
|--|------|------------|---------|
| => fil caplus | | SINCE FILE | TOTAL |
| COST IN U.S. DOLLARS | | ENTRY | SESSION |
| FULL ESTIMATED COST | 0.90 | | 240.65 |
| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | | SINCE FILE | TOTAL |
| CA SUBSCRIBER PRICE | 0.00 | ENTRY | SESSION |
| | | | -7.50 |

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FILE COVERS 1907 - 20 Jan 2006 VOL 144 ISS 4
FILE LAST UPDATED: 18 Jan 2006 (20060118/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

<http://www.cas.org/infopolicy.html>

=> s oxidiz?
L26 394449 OXIDIZ?

=> s l26 and hydrocarbon
323712 HYDROCARBON
324371 HYDROCARBONS
499122 HYDROCARBON
(HYDROCARBON OR HYDROCARBONS)
L27 17243 L26 AND HYDROCARBON

=> s l27 and chromium
353366 CHROMIUM
74 CHROMIUMS
353370 CHROMIUM
(CHROMIUM OR CHROMIUMS)
L28 392 L27 AND CHROMIUM

=> s l28 and hemiacetal
3691 HEMIACETAL
1145 HEMIACETALS
4307 HEMIACETAL
(HEMIACETAL OR HEMIACETALS)
L29 1 L28 AND HEMIACETAL

=> d

L29 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2004:372938 CAPLUS
DN 140:391402
TI Catalytic oxidation of C-H bonds and its application to
α-hydroxylation of cyclic steroidal ethers
IN Fuchs, Philip; Lee, Seongmin
PA USA
SO U.S. Pat. Appl. Publ., 38 pp.
CODEN: USXXCO
DT Patent
LA English
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----------------------|------|----------|-----------------|----------|
| PI US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |
| PRAI US 2002-403498P | P | 20020814 | | |
| OS CASREACT | | | 140:391402 | |

```
=> s 128 and periodic acid
    89995 PERIODIC
        7 PERIODICS
    89998 PERIODIC
        (PERIODIC OR PERIODICS)
    4087882 ACID
    1507158 ACIDS
    4573859 ACID
        (ACID OR ACIDS)
    5770 PERIODIC ACID
        (PERIODIC(W) ACID)
L30          4 L28 AND PERIODIC ACID
```

```
=> s 130 and chromoyl diacetate
    2 CHROMOYL
    38732 DIACETATE
    1884 DIACETATES
    39549 DIACETATE
        (DIACETATE OR DIACETATES)
    1 CHROMOYL DIACETATE
        (CHROMOYL(W) DIACETATE)
L31          0 L30 AND CHROMOYL DIACETATE
```

```
=> d 130 104
    4 ANSWERS ARE AVAILABLE.  SPECIFIED ANSWER NUMBER EXCEEDS ANSWER SET SIZE
The answer numbers requested are not in the answer set.
ENTER ANSWER NUMBER OR RANGE (1):1-4
```

L30 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2004:372938 CAPLUS
DN 140:391402
TI Catalytic oxidation of C-H bonds and its application to
α-hydroxylation of cyclic steroidal ethers
IN Fuchs, Philip; Lee, Seongmin
PA USA
SO U.S. Pat. Appl. Publ., 38 pp.
CODEN: USXXCO
DT Patent
LA English
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------|------|----------|-----------------|----------|
| PI US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |

PRAI US 2002-403498P
OS CASREACT 140:391402

L30 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2003:591044 CAPLUS
DN 139:122002
TI Mediated electrochemical oxidation of destruction of sharps
IN Carson, Roger W.; Bremer, Bruce W.
PA The C & M Group, Llc, USA
SO PCT Int. Appl., 104 pp.
CODEN: PIXXD2
DT Patent
LA English
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------|----------|
| PI WO 2003061714 | A2 | 20030731 | WO 2003-US2151 | 20030124 |
| WO 2003061714 | A3 | 20031113 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, U2, VC, VN, YU, ZA, ZM, ZW
RW: GH, GM, KE, LS, MM, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| US 2005103642 | A1 | 20050519 | US 2003-502439 | 20030124 |
| PRAI US 2002-350352P | P | 20020124 | | |
| WO 2003-US2151 | W | 20030124 | | |

L30 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2002:594799 CAPLUS
DN 137:154689
TI Method of synthesizing α-ketol unsaturated fatty acids
IN Yokokawa, Yoshihiro; Kobayashi, Koji; Yamamura, Shosuke
PA Shiseido Co., Ltd., Japan
SO PCT Int. Appl., 46 pp.
CODEN: PIXXD2
DT Patent
LA Japanese
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------|----------|
| PI WO 2002060850 | A1 | 20020808 | WO 2001-JP660 | 20010131 |
| W: AU, CA, CN, KR, US
RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR
CA 2397868 AA 20020808 CA 2001-2397868 . 20010131
EP 1357106 A1 20031029 EP 2001-902700 20010131
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI, CY, TR
US 2002156304 A1 20021024 US 2002-110239 20020410
US 6605741 B2 20030812 | | | | |

PRAI WO 2001-JP660
OS CASREACT 137:154689; MARPAT 137:154689
RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L30 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2006 ACS on STN
AN 2001:292804 CAPLUS
DN 135:137265
TI Chromium(VI) oxide-catalyzed oxidation of arenes with
periodic acid
AU Yamazaki, S.
CS 150 Futagami, Toyama Industrial Technology Center, Toyama, Takaoka,
933-0981, Japan
SO Tetrahedron Letters (2001), 42(19), 3355-3357
CODEN: TELEAY; ISSN: 0040-4039
PB Elsevier Science Ltd.
DT Journal
LA English
OS CASREACT 135:137265
RE.CNT 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d his

(FILE 'HOME' ENTERED AT 06:47:36 ON 20 JAN 2006)

FILE 'CAPLUS' ENTERED AT 06:48:22 ON 20 JAN 2006

L1 32965 S OXIDIZE
L2 20 S L1 AND HEMIACETAL
L3 0 S L2 AND CHROMIUM
L4 353370 S CHROMIUM
L5 1290 S L4 AND OXIDANT
L6 3 S L5 AND HEMIACETAL
L7 1 S US2004087820/PN
L8 867233 S OXIDATION
L9 28146 S L8 AND CHROMIUM
L10 734 S L9 AND OXIDANT
L11 6 S L10 AND STEROID

FILE 'REGISTRY' ENTERED AT 06:51:35 ON 20 JAN 2006

L12 STRUCTURE UPLOADED
L13 0 S L12
L14 22 S L12 FULL

FILE 'CAPLUS' ENTERED AT 06:52:15 ON 20 JAN 2006

L15 13 S L14
L16 3 S L15 AND CHROMIUM

FILE 'STNGUIDE' ENTERED AT 06:53:13 ON 20 JAN 2006

L17 0 S SATALYTIC CHROMOYL DIACETATE
L18 0 S CATALYTIC CHROMOYL DIACETATE

FILE 'CAPLUS' ENTERED AT 06:59:16 ON 20 JAN 2006

4573859 ACID
(ACID OR ACIDS)

5770 PERIODIC ACID
(PERIODIC (W) ACID)

L33 0 L32 AND PERIODIC ACID

=> s l32 and tetrabutylammonium periodate

22113 TETRABUTYLMAMMONIUM

14923 PERIODATE

1041 PERIODATES

15260 PERIODATE

(PERIODATE OR PERIODATES)

60 TETRABUTYLMAMMONIUM PERIODATE

(TETRABUTYLMAMMONIUM (W) PERIODATE)

L34 0 L32 AND TETRABUTYLMAMMONIUM PERIODATE

=> s l32 and hydrogen peroxide

903744 HYDROGEN

5684 HYDROGENS

906931 HYDROGEN

(HYDROGEN OR HYDROGENS)

197917 PEROXIDE

45272 PEROXIDES

215601 PEROXIDE

(PEROXIDE OR PEROXIDES)

105285 HYDROGEN PEROXIDE

(HYDROGEN (W) PEROXIDE)

L35 1 L32 AND HYDROGEN PEROXIDE

=> d

L35 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
AN 1998:613842 CAPLUS
DN 129:304397
TI Method and apparatus for manufacture organic sulfur compounds from sulfur
compounds in petroleum
IN Funakoshi, Izumi
PA Japan
SO Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--------------------|------|----------|-----------------|----------|
| PI JP 10251665 | A2 | 19980922 | JP 1997-82400 | 19970317 |
| PRAI JP 1997-82400 | | | | |

=> s 132 and diacyl peroxide
 5429 DIACYL
 13 DIACYLS
 5436 DIACYL
 (DIACYL OR DIACYLS)
197917 PEROXIDE
 45272 PEROXIDES
215601 PEROXIDE
 (PEROXIDE OR PEROXIDES)
 847 DIACYL PEROXIDE
 (DIACYL(W) PEROXIDE)
L36 0 L32 AND DIACYL PEROXIDE

=> d his

 (FILE 'HOME' ENTERED AT 06:47:36 ON 20 JAN 2006)

FILE 'CAPPLUS' ENTERED AT 06:48:22 ON 20 JAN 2006
L1 32965 S OXIDIZE
L2 20 S L1 AND HEMIACETAL
L3 0 S L2 AND CHROMIUM
L4 353370 S CHROMIUM
L5 1290 S L4 AND OXIDANT
L6 3 S L5 AND HEMIACETAL
L7 1 S US2004087820/PN
L8 867233 S OXIDATION
L9 28146 S L8 AND CHROMIUM
L10 734 S L9 AND OXIDANT
L11 6 S L10 AND STEROID

FILE 'REGISTRY' ENTERED AT 06:51:35 ON 20 JAN 2006
L12 STRUCTURE uploaded
L13 0 S L12
L14 22 S L12 FULL

FILE 'CAPPLUS' ENTERED AT 06:52:15 ON 20 JAN 2006
L15 13 S L14
L16 3 S L15 AND CHROMIUM

FILE 'STNGUIDE' ENTERED AT 06:53:13 ON 20 JAN 2006
L17 0 S SATALYTIC CHROMOYL DIACETATE
L18 0 S CATALYTIC CHROMOYL DIACETATE

FILE 'CAPPLUS' ENTERED AT 06:59:16 ON 20 JAN 2006
L19 1 S CATALYTIC CHROMOYL DIACETATE

FILE 'STNGUIDE' ENTERED AT 06:59:51 ON 20 JAN 2006
L20 0 S HYDROXYLATEION
L21 0 S HYDROXYLATION
L22 0 S OXIDIZ?
L23 0 S OXIDIZ
L24 0 S OXIDIZ?
L25 3 S (OXIDIZE OR OXIDIZING OR OXIDATION)

FILE 'CAPPLUS' ENTERED AT 07:08:35 ON 20 JAN 2006
L26 394449 S OXIDIZ?
L27 17243 S L26 AND HYDROCARBON
L28 392 S L27 AND CHROMIUM
L29 1 S L28 AND HEMIACETAL
L30 4 S L28 AND PERIODIC ACID

L31 0 S L30 AND CHROMOYL DIACETATE
L32 38 S L28 AND CRO3
L33 0 S L32 AND PERIODIC ACID
L34 0 S L32 AND TETRABUTYLMONIUM PERIODATE
L35 1 S L32 AND HYDROGEN PEROXIDE
L36 0 S L32 AND DIACYL PEROXIDE

=> s l28 and chromoyl chloride
 2 CHROMOYL
 1059143 CHLORIDE
 155322 CHLORIDES
 1130146 CHLORIDE
 (CHLORIDE OR CHLORIDES)
 1 CHROMOYL CHLORIDE
 (CHROMOYL (W) CHLORIDE)
L37 0 L28 AND CHROMOYL CHLORIDE

=> s l28 and chromoyl diacetate
 2 CHROMOYL
 38732 DIACETATE
 1884 DIACETATES
 39549 DIACETATE
 (DIACETATE OR DIACETATES)
 1 CHROMOYL DIACETATE
 (CHROMOYL (W) DIACETATE)
L38 0 L28 AND CHROMOYL DIACETATE

=> s l28 and chromoyl bistrifluoroacetate
 2 CHROMOYL
 112 BISTRIFLUOROACETATE
 4 BISTRIFLUOROACETATES
 115 BISTRIFLUOROACETATE
 (BISTRIFLUOROACETATE OR BISTRIFLUOROACETATES)
 0 CHROMOYL BISTRIFLUOROACETATE
 (CHROMOYL (W) BISTRIFLUOROACETATE)
L39 0 L28 AND CHROMOYL BISTRIFLUOROACETATE

=> s l28 and chromium [VI] oxidant
 353366 CHROMIUM
 74 CHROMIUMS
 353370 CHROMIUM
 (CHROMIUM OR CHROMIUMS)
 208629 VI
 55738 VIS
 264078 VI
 (VI OR VIS)
 43065 OXIDANT
 15958 OXIDANTS
 53405 OXIDANT
 (OXIDANT OR OXIDANTS)
 8 CHROMIUM [VI] OXIDANT
 (CHROMIUM (W) VI (W) OXIDANT)
L40 1 L28 AND CHROMIUM [VI] OXIDANT

=> d

L40 ANSWER 1 OF 1 CAPIUS COPYRIGHT 2006 ACS on STN
AN 2004:372938 CAPIUS
DN 140:391402
TI Catalytic oxidation of C-H bonds and its application to
α-hydroxylation of cyclic steroidal ethers
IN Fuchs, Philip; Lee, Seongmin
PA USA
SO U.S. Pat. Appl. Publ., 38 pp.
CODEN: USXXCO
DT Patent
LA English
FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----------------------|------|------------|-----------------|----------|
| PI US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |
| PRAI US 2002-403498P | P | 20020814 | | |
| OS CASREACT | | 140:391402 | | |

=> log y
COST IN U.S. DOLLARS

| | SINCE FILE ENTRY | TOTAL SESSION |
|---------------------|------------------|---------------|
| FULL ESTIMATED COST | 61.44 | 302.09 |

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

| | SINCE FILE ENTRY | TOTAL SESSION |
|---------------------|------------------|---------------|
| CA SUBSCRIBER PRICE | 0.00 | -7.50 |

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| Ref # | Hits | Search Query | DBs | Default Operator | Plurals | Time Stamp |
|-------|------|-----------------|--|------------------|---------|------------------|
| L1 | 60 | (540/19).CCLS. | US-PGPUB;
USPAT;
EPO;
DERWENT | OR | OFF | 2006/01/20 08:01 |
| L2 | 61 | (549/344).CCLS. | US-PGPUB;
USPAT;
EPO;
DERWENT | OR | OFF | 2006/01/20 08:01 |

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PASSWORD :

TERMINAL (ENTER 1, 2, 3, OR ?):2

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NEWS 2 "Ask CAS" for self-help around the clock
NEWS 3 DEC 05 CASREACT(R) - Over 10 million reactions available
NEWS 4 DEC 14 2006 MeSH terms loaded in MEDLINE/LMEDLINE
NEWS 5 DEC 14 2006 MeSH terms loaded for MEDLINE file segment of TOXCENTER
NEWS 6 DEC 14 CA/CAplus to be enhanced with updated IPC codes
NEWS 7 DEC 21 IPC search and display fields enhanced in CA/CAplus with the
IPC reform
NEWS 8 DEC 23 New IPC8 SEARCH, DISPLAY, and SELECT fields in USPATFULL/
USPAT2
NEWS 9 JAN 13 IPC 8 searching in IFIPAT, IFIUDB, and IFICDB
NEWS 10 JAN 13 New IPC 8 SEARCH, DISPLAY, and SELECT enhancements added to
INPADOC
NEWS 11 JAN 17 Pre-1988 INPI data added to MARPAT
NEWS 12 JAN 17 IPC 8 in the WPI family of databases including WPIFV

NEWS EXPRESS JANUARY 03 CURRENT VERSION FOR WINDOWS IS V8.01,
CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
AND CURRENT DISCOVER FILE IS DATED 19 DECEMBER 2005.
V8.0 USERS CAN OBTAIN THE UPGRADE TO V8.01 AT
<http://download.cas.org/express/v8.0-Discover/>

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NEWS PHONE Direct Dial and Telecommunication Network Access to STN
NEWS WWW CAS World Wide Web Site (general information)

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STRUCTURE FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2
DICTIONARY FILE UPDATES: 18 JAN 2006 HIGHEST RN 872163-75-2

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TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

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*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
*

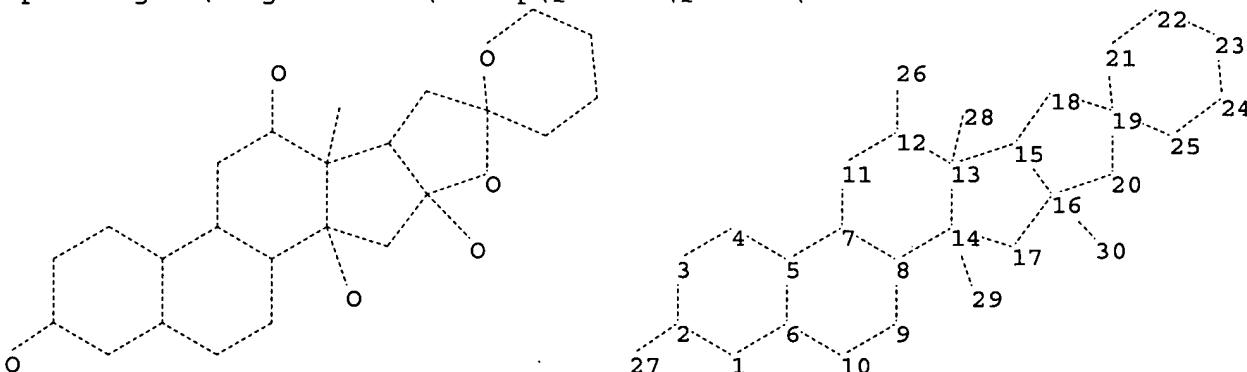
Structure search iteration limits have been increased. See HELP SLIMITS for details.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=>

Uploading C:\Program Files\Stnexp\Queries\QUERIES\10636129.str



chain nodes :

26 27 28 29 30

ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
24 25

chain bonds :

2-27 12-26 13-28 14-29 16-30

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12 12-13
13-14 13-15 14-17 15-16 15-18 16-17 16-20 18-19 19-20 19-21 19-25 21-22
22-23 23-24 24-25

exact/norm bonds :

1-2 1-6 2-3 2-27 3-4 4-5 5-6 5-7 6-10 7-8 7-11 8-9 8-14 9-10 11-12
12-13 12-26 13-14 13-15 13-28 14-17 14-29 15-16 15-18 16-17 16-20 16-30
18-19 19-20 19-21 19-25 21-22 22-23 23-24 24-25

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:Atom 25:Atom 26:CLASS 27:CLASS 28:CLASS
29:CLASS 30:CLASS

L1 STRUCTURE UPLOADED

=> d
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *
Structure attributes must be viewed using STN Express query preparation.

=> s 11
SAMPLE SEARCH INITIATED 08:47:43 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 17 TO ITERATE

100.0% PROCESSED 17 ITERATIONS 0 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 93 TO 587
PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s 11 full
FULL SEARCH INITIATED 08:47:46 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 464 TO ITERATE

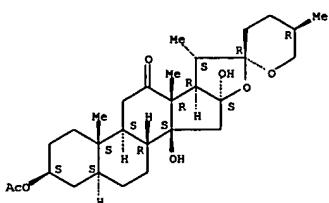
100.0% PROCESSED 464 ITERATIONS 1 ANSWERS
SEARCH TIME: 00.00.01

L3 1 SEA SSS FUL L1

=> d

L3 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2006 ACS on STN
RN 571185-76-7 REGISTRY
ED Entered STN: 22 Aug 2003
CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-,
(3B,5a,14B,25R)- (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C29 H44 O7
SR CA
LC STN Files: CA, CAPLUS, CASREACT, USPATFULL

Absolute stereochemistry.



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

3 REFERENCES IN FILE CA (1907 TO DATE)
3 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> fil caplus
COST IN U.S. DOLLARS
FULL ESTIMATED COST

| SINCE FILE ENTRY | TOTAL SESSION |
|------------------|---------------|
| 168.84 | 169.05 |

FILE 'CAPLUS' ENTERED AT 08:47:52 ON 20 JAN 2006
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FILE COVERS 1907 - 20 Jan 2006 VOL 144 ISS 5
FILE LAST UPDATED: 19 Jan 2006 (20060119/ED)

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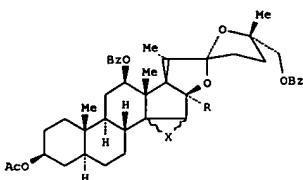
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L4 3 L3
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L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:372938 CAPLUS
 DOCUMENT NUMBER: 140:391402
 TITLE: Catalytic oxidation of C-H bonds and its application to α -hydroxylation of cyclic steroidal ethers
 INVENTOR(S): Fuchs, Philip; Lee, Seongmin
 PATENT ASSIGNEE(S): USA
 SOURCE: U.S. Pat. Appl. Publ., 38 pp.
 CODEN: USXXCO
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|------|----------|-----------------|------------|
| US 2004087820 | A1 | 20040506 | US 2003-636129 | 20030807 |
| PRIORITY APPLN. INFO.: | | | US 2002-403498P | P 20020814 |

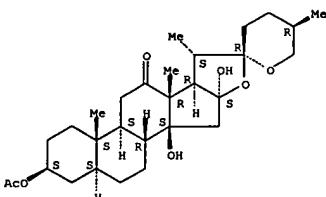
OTHER SOURCE(S): CASREACT 140:391402
 GI



AB The invention provides a catalytic, chemospecific and stereospecific method of oxidizing a wide variety of substrates without unwanted side reactions. Essentially, the method of the instant invention, under relatively mild reaction conditions, catalytically, stereospecifically and chemospecifically inserts oxygen into a hydrocarbon C-H bond. Oxidation (oxygen insertion) at a tertiary C-H bond to form an alc. (and in some cases a hemiacetal) at the tertiary carbon is favored. The stereochemistry of an oxidized tertiary carbon is preserved. Ketones are formed by oxidizing a secondary C-H bond and ring-cleaved diones are formed by oxidizing cis tertiary C-H bonds. Thus, epoxysalic. I ($X = O$, $R = OH$) was prepared by reacting spiroketal compound I ($X = \text{bond}$, $R = H$) in an anhydrous solvent with chromium [VI] oxidant and a co-oxidant at a reaction temperature between about -100° C to about 0° C and a reaction time of between about 30 min to about 3 h. The method is useful in the synthesis of intermediates appropriate for preparation of analogs of the

L4 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2004:261227 CAPLUS
 DOCUMENT NUMBER: 140:423861
 TITLE: An Efficient C-H Oxidation Protocol for α -Hydroxylation of Cyclic Steroidal Ethers
 AUTHOR(S): Lee, Seongmin; Fuchs, Philip L.
 CORPORATE SOURCE: Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA
 SOURCE: Organic Letters (2004), 6(9), 1437-1440
 CODEN: ORLEF7; ISSN: 1523-7060
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 140:423861
 AB Various C-16 hydroxy steroids have been prepared with the aid of CrO₃/Bu₄NIO₄. Out of the two possible reaction courses, transition state B is favored because of less steric interference between substrate and CrO₄. Thus, C-H bonds at C-16 are oxidized selectively.
 IT 571185-76-7P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (regio-, stereo- and chemoselective α -hydroxylation of cyclic steroidal ethers using CrO₃/Bu₄NIO₄)
 RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



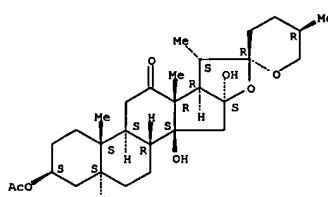
REFERENCE COUNT: 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN (Continued)
 ACCESSION NUMBER: 2003:435935 CAPLUS
 DOCUMENT NUMBER: 139:149817
 TITLE: New Oxidative Tools for the Functionalization of the Cephalostatin North 1 Hemisphere
 AUTHOR(S): Lee, Jong Seok; Fuchs, Philip L.
 CORPORATE SOURCE: Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA
 SOURCE: Organic Letters (2003), 5(13), 2247-2250
 CODEN: ORLEF7; ISSN: 1523-7060
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 139:149817
 GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB New oxidative tools for the functionalization of the cephalostatin 1 northern hemisphere have been developed. Dimethylidioxirane (DMDO) C-H oxidation of ketone I ($Y=B-OH$, $Z=H$) to hemiketal I ($Y=B-OH$, $Z=OH$) (82%), bis-dehydration to vinyl ether II (77%), and DMDO again provides C-23 axial alc. III (98%). Routine processing, including a double-stereoselective Sharpless AD reaction ($de > 98\%$), gives alc. IV. Compound IV, bearing a C-23 silyl ether, undergoes Suarez hypoiodite oxidative cyclization to generate unnatural spiroketal V.
 IT 571185-76-7P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (new oxidative tools for the functionalization of the cephalostatin 1 northern hemisphere)
 RN 571185-76-7 CAPLUS
 CN Spirostan-12-one, 3-(acetoxy)-14,16-dihydroxy-, (3 β ,5 α ,14 β ,25R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

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